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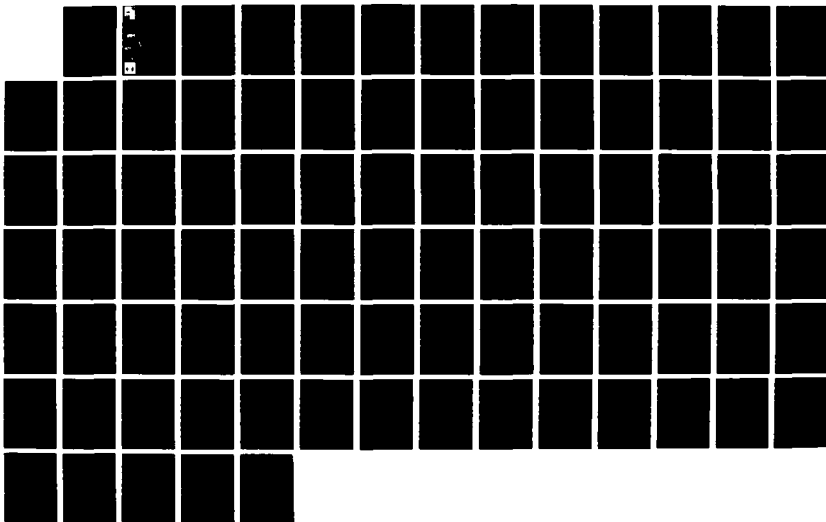
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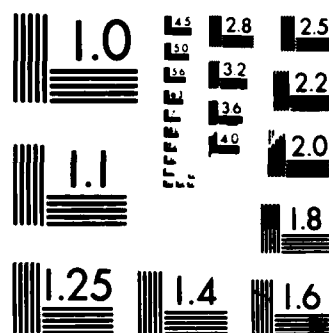
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ENVIRONMENTAL EFFECTS  
OF DREDGING PROGRAMS

MISCELLANEOUS PAPER D-87-3

REGULATORY IDENTIFICATION OF PETROLEUM  
HYDROCARBONS IN DREDGED MATERIAL

PROCEEDINGS OF A WORKSHOP

Compiled by

Joan U. Clarke, Alfreda B. Gibson

Environmental Laboratory

DEPARTMENT OF THE ARMY

Waterways Experiment Station, Corps of Engineers  
PO Box 631, Vicksburg, Mississippi 39180-0631

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March 1987

Final Report

Approved For Public Release; Distribution Unlimited

Prepared for US Army Engineer District, New York  
New York, New York 10278-0090

and US Army Engineer District, Chicago  
Chicago, Illinois 60604-1797

87 5 6 00 5

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SECURITY CLASSIFICATION OF THIS PAGE

REPORT DOCUMENTATION PAGE				Form Approved OMB No 0704-0188 Exp Date Jun 30, 1986	
1a REPORT SECURITY CLASSIFICATION <b>Unclassified</b>			1b RESTRICTIVE MARKINGS		
2a SECURITY CLASSIFICATION AUTHORITY			3 DISTRIBUTION/AVAILABILITY OF REPORT <b>Approved for public release; distribution unlimited.</b>		
2b DECLASSIFICATION/DOWNGRADING SCHEDULE					
4 PERFORMING ORGANIZATION REPORT NUMBER(S) <b>Miscellaneous Paper D-87-3</b>			5 MONITORING ORGANIZATION REPORT NUMBER(S)		
6a. NAME OF PERFORMING ORGANIZATION <b>USAEWES Environmental Laboratory</b>		6b OFFICE SYMBOL (If applicable)	7a NAME OF MONITORING ORGANIZATION		
6c. ADDRESS (City, State, and ZIP Code) <b>PO Box 631 Vicksburg, MS 39180-0631</b>			7b. ADDRESS (City, State, and ZIP Code)		
8a. NAME OF FUNDING/SPONSORING ORGANIZATION <b>See reverse</b>		8b OFFICE SYMBOL (If applicable)	9 PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER		
8c. ADDRESS (City, State, and ZIP Code) <b>New York, NY 10278-0090; Chicago, IL 60604-1797</b>			10. SOURCE OF FUNDING NUMBERS		
			PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO.
					WORK UNIT ACCESSION NO.
11 TITLE (Include Security Classification) <b>Regulatory Identification of Petroleum Hydrocarbons in Dredged Material; Proceedings of a Workshop</b>					
12 PERSONAL AUTHOR(S) <b>Clarke, Joan U.; Gibson, Alfreda B.</b>					
13a TYPE OF REPORT <b>Final report</b>		13b TIME COVERED FROM _____ TO _____		14 DATE OF REPORT (Year, Month, Day) <b>March 1987</b>	
				15 PAGE COUNT <b>87</b>	
16 SUPPLEMENTARY NOTATION <b>Available from National Technical Information Service, 5285 Port Royal Road, Springfield, VA 22161.</b>					
17 COSATI CODES			18 SUBJECT TERMS (Continue on reverse if necessary and identify by block number)		
FIELD      GROUP      SUB-GROUP					
			<b>See reverse</b>		
19 ABSTRACT (Continue on reverse if necessary and identify by block number) <p>A 3-day workshop on the regulatory evaluation of petroleum hydrocarbons in dredged material was conducted 13-15 May 1986 at the US Army Engineer Waterways Experiment Station (WES), Vicksburg, Miss. The workshop, organized and chaired by the Environmental Laboratory, WES, was held at the request of US Army Engineer Districts, New York and Chicago, for assistance in evaluating contaminated dredged material. This document is a detailed summary of the workshop proceedings.</p> <p>Workshop participants, who represented Government agencies, private industry, and academia, were selected for their expertise in various aspects of the environmental chemistry and biological effects of petroleum hydrocarbons. Prior to the workshop, participants were asked to submit a brief outline of their ideas on selecting key compounds that would be of most use in the regulatory evaluation of petroleum hydrocarbons in dredged material. These preworkshop inputs were used to finalize the agenda and to help the participants become acquainted with each other's perspectives. (Continued)</p>					
20 DISTRIBUTION/AVAILABILITY OF ABSTRACT <input checked="" type="checkbox"/> UNCLASSIFIED/UNLIMITED <input type="checkbox"/> SAME AS RPT <input type="checkbox"/> DTIC USERS			21 ABSTRACT SECURITY CLASSIFICATION <b>Unclassified</b>		
22a NAME OF RESPONSIBLE INDIVIDUAL			22b TELEPHONE (Include Area Code)		22c OFFICE SYMBOL

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SECURITY CLASSIFICATION OF THIS PAGE

8a. FUNDING/SPONSORING ORGANIZATION (Continued).

US Army Engineer District, New York;  
US Army Engineer District, Chicago

18. SUBJECT TERMS (Continued).

Petroleum hydrocarbons	Bioaccumulation tests
Dredged material	Bioavailability
Polycyclic aromatic hydrocarbons (PAH)	Regulatory evaluation
Priority pollutant PAH	Tiered testing
Acute toxicity tests	QA/QC
Sediment analysis	

19. ABSTRACT (Continued).

The workshop format consisted of brief topic introductions by each participant, followed by roundtable discussions. The discussions culminated in the recommendation of specific hydrocarbon compounds and the development of a suggested tiered testing approach for regulatory evaluation of hydrocarbon-contaminated dredged material. The compounds selected were 15 priority pollutant polycyclic aromatic hydrocarbons: acenaphthene, acenaphthylene, anthracene, benz(a)anthracene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(g,h,i)perylene, benzo(a)pyrene, chrysene, dibenz(a,h)anthracene, fluoranthene, fluorene, indeno(1,2,3-cd)pyrene, phenanthrene, and pyrene. The tiered testing approach consisted of first-tier acute toxicity tests and sediment analysis for the key hydrocarbons, followed by second-tier 10-day bioaccumulation tests. Other classes of hydrocarbons and biological tests were recommended for further research, with possible future inclusion in the evaluation scheme.

Following the workshop, all participants were provided with a copy of the draft proceedings. Their comments were solicited and incorporated into the final edition prior to publication.

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## PREFACE

This report summarizes the proceedings of a workshop held 13-15 May 1986 at the US Army Engineer Waterways Experiment Station (WES), Vicksburg, Miss. The workshop was held in response to requests by the US Army Engineer Districts (USAED), New York and Chicago, for assistance in identifying particular compounds, from the complex petroleum hydrocarbon mixtures associated with sediments, that are most appropriate for analysis as a basis for regulation of dredged material disposal.

To identify key compounds for environmentally sound evaluations of dredged material, a number of widely recognized authorities with extensive expertise in the analysis and potential environmental impacts of petroleum hydrocarbons in sediment were selected to participate in the workshop. These experts represented Government agencies, academia, and private industry in the United States and Canada.

Financial support for travel and preparation of the report was provided by the USAED, New York, to the WES Environmental Laboratory (EL) through an Intra-Army Order for Reimbursable Services.

The workshop proceedings were compiled by Ms. Joan U. Clarke, who served as Workshop Chairperson, and Ms. Alfreda B. Gibson of the Ecosystem Research and Simulation Division (ERSD), EL. The compilers gratefully acknowledge the coordinating efforts of Messrs. James Mansky and John Tavoraro of the USAED, New York, and Mr. Jan Miller of the USAED, Chicago. The outstanding editorial services of Ms. Dorothy Booth of the Environmental Information Analysis Center, EL, and Ms. Jessica Ruff of the WES Information Products Division are appreciated.

The compilers are also grateful to all of the workshop participants who reviewed this report and provided written comments and clarifications. Dr. John Stegeman of the Woods Hole Oceanographic Institution, who was unable to attend the workshop, also reviewed this report. Where appropriate, his comments have been included in the text.

This project was conducted under the general supervision of Dr. Richard K. Peddicord, Team Leader, Biological Evaluation and Criteria Team, and Dr. Charles R. Lee, Group Chief, Contaminant Mobility and Regulatory Criteria Group, ERSD. Mr. Donald L. Robey was Chief, ERSD, and Dr. John Harrison was Chief, EL.

COL Allen F. Grum, USA, was the previous Director of WES. COL Dwayne G. Lee, CE, is the present Commander and Director. Dr. Robert W. Whalin is Technical Director.

This report should be cited as follows:

Clarke, Joan U., and Gibson, Alfreda B. 1987. "Regulatory Identification of Petroleum Hydrocarbons in Dredged Material; Proceedings of a Workshop," Miscellaneous Paper D-87-3, US Army Engineer Waterways Experiment Station, Vicksburg, Miss.

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## AGENDA

### Monday, May 12, 1986

7:00-9:00 pm Plenary session - Holiday Inn, Mississippi Room

### Tuesday, May 13, 1986 - Environmental Laboratory Classroom 1

8:15 am Opening remarks - Dr. Robert Whalin  
Introduction and background - Dr. Richard Peddicord  
10:00 am Break  
10:15 am Environmental chemistry (overview) and analytical techniques - Dr. Jim Petty  
Environmental fate - Dr. Scott MacKnight  
Transport/partitioning - Dr. John McCarthy  
Degradation (abiotic) - Dr. Lee Wolfe  
Degradation (microbial) - Mr. Michael Heitkamp  
Bioavailability - Dr. Joseph O'Connor  
Bioaccumulation - Mr. Victor McFarland  
12 noon Lunch  
1:00 pm Environmental chemistry (discussion of fate)  
2:45 pm Break  
3:00 pm Environmental chemistry (discussion of bioavailability)  
4:30 pm Transportation to hotel

### Wednesday, May 14, 1986 - Environmental Laboratory Classroom 1

8:15 am Biological effects (overview) - Dr. Tom Dillon  
Toxicology - Dr. Peter Landrum  
Biochemistry/physiology - Dr. Richard Lee  
Metabolism - Dr. John Stein  
Discussion of toxicology  
10:00 am Break  
10:15 am Biological effects (discussion of physiology)  
12 noon Lunch  
1:00 pm Biological effects (discussion of metabolism)  
2:45 pm Break  
3:00 pm Quantitative structure-activity relationships (QSAR) - Dr. Robert Lipnick  
Discussion of QSAR  
4:30 pm Transportation to hotel

### Thursday, May 15, 1986 - Environmental Laboratory Classroom 1

8:15 am Refine lists of important petroleum hydrocarbons  
10:00 am Break  
10:15 am Summary and conclusions  
11:15 am Consensus luncheon - Walnut Hills  
1:00 pm Transportation to airport

## ATTENDEES

### Workshop Chairperson

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Dr. Peter Landrum Great Lakes Environmental Research Laboratory 2300 Washtenaw Ave. Ann Arbor, MI 48104-4590 (FTS) 378-2276	Aquatic toxicology, bioavailability; environmental chemistry, fate of organic pollutants
Dr. Richard Lee Skidaway Institute of Oceanography University System of Georgia PO Box 13687 Savannah, GA 31416 912-356-2494	Aquatic toxicology, bioaccumulation
Dr. Robert Lipnick Office of Toxic Substances EPA Mail Code TS-796 Washington, DC 20460 (FTS) 382-4274	Physical organic chemistry, quantita- tive structure-activity relationships
Dr. Scott MacKnight OceanChem group Suite 46, 1000 Windmill Road Dartmouth, Nova Scotia Canada BSB 1L7 902-463-0114	Chemical oceanography, environmental impacts of contaminants in dredged material
Dr. John McCarthy Oak Ridge National Laboratory PO Box X Oak Ridge, TN 37831 (FTS) 626-6606	Aquatic toxicology, environmental partitioning, bioavailability, metabolism

<u>Technical Participants</u>	<u>Area of Expertise</u>
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Dr. Jim Petty Columbia National Fisheries Research Laboratory R.R. 1, New Haven School Road Columbia, MO 65201 (FTS) 276-5399	Organic analytical chemistry, environ- mental contamination
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REGULATORY IDENTIFICATION OF PETROLEUM  
HYDROCARBONS IN DREDGED MATERIAL

PROCEEDINGS OF A WORKSHOP

PART I: BACKGROUND

Summary of Scope of Work

1. This section summarizes the Scope of Work, which is provided as Appendix A.

2. The term "petroleum hydrocarbons" includes a large number of compounds, some of which are recognized as potentially serious environmental threats. Hundreds of these compounds have been identified in sediment, water, and tissue samples. They span a wide range of water solubility, persistence, bioavailability, toxicity, bioaccumulation potential, carcinogenicity, and overall biological importance.

3. Analysis of petroleum hydrocarbons as "oil and grease" or even as "total petroleum hydrocarbons" or other summary type measures cannot provide sufficient information to accurately evaluate the potential for environmental impact of a sample whose significance is determined by its particular mix of these compounds. On the other hand, qualitative and quantitative analyses of all petroleum compounds present would be virtually impossible. Even a relatively comprehensive analysis would be too time-consuming and expensive, and would produce an excessive volume of data to be reviewed as part of the regulatory process. Thus, an intermediate approach is needed for adequate and informed regulatory evaluations of potential toxic impact of petroleum hydrocarbons in dredged material.

4. Dr. Richard Peddicord of the US Army Engineer Waterways Experiment Station (WES) was contacted by Mr. James Mansky of the US Army Engineer District (USAED), New York, and Mr. Jan Miller of the USAED, Chicago, for assistance in identifying particular components of the petroleum hydrocarbon mixture that could be most appropriate for analysis as a basis for environmental regulation of dredged material disposal. As demonstrated in the past, one productive way to arrive at consensus findings on complex scientific issues is through a technical working group of experts. A group of widely

recognized authorities with expertise in environmental impacts of petroleum hydrocarbons in sediment was identified. From this group approximately 10 scientists from Government, academia, and the private sector, who had knowledge of the chemistry and the biological effects of petroleum hydrocarbons, dredging, and the dredged material regulatory process, were selected to participate. Representatives of the USAE Districts, New York and Chicago, were also included. Technical participants were asked to submit a written summary of their ideas concerning which petroleum hydrocarbons would be most appropriate for use in regulatory evaluations and to be prepared to justify their inputs at the workshop.

5. At the conclusion of the workshop, a report describing the objective, methods, findings, and conclusions was prepared in the form of a WES Miscellaneous Paper. Conclusions were technically supported on the basis of the consensus of the recognized authorities participating in the workshop. A draft report was submitted to the USAE Districts, New York and Chicago, for review and comment prior to the preparation of the Miscellaneous Paper. Sufficient copies of the Miscellaneous Paper will be published for transmittal to the sponsors and for limited distribution.

#### Preworkshop Input

6. To further refine the agenda of the workshop and to acquaint the participants with each other's perspectives, preworkshop input was sought from each participant. The participants were asked to submit a brief written summary or outline of their ideas and rationale concerning which key petroleum hydrocarbons would be of most use to regulators in evaluating petroleum in dredged material. Copies of all inputs were distributed to the participants prior to the workshop.

7. The preworkshop inputs are provided as Appendix B. Also included are inputs from two petroleum hydrocarbons experts who were unable to attend due to scheduling conflicts.

8. A number of common themes and important recommendations that emerged from the preworkshop inputs are summarized below. All of these themes were discussed at length during the workshop, and the results of the discussions are presented in Part II. The recommendations presented in the preworkshop

inputs and summarized below were not necessarily adopted as consensus agreements during the workshop.

- a. The currently used "oil and grease" test is inadequate but, on the other hand, attempting to analyze sediments for all petroleum hydrocarbons would be expensive and the data would be virtually uninterpretable. Therefore, a limited number of select compounds or classes of compounds should be analyzed. This would be analogous to the present use of polychlorinated biphenyls (PCB) as a "surrogate" compound for organohalogens in dredged material.
- b. It was generally agreed that the polycyclic aromatic hydrocarbons (PAH) are the class of hydrocarbons most likely to be of ecological importance as sediment contaminants. This class typically is considered to include aromatic hydrocarbons (e.g., pyrene) and various nitrogen, oxygen, or sulfur substituted aromatic compounds (e.g., carbazole, dibenzothiophene, etc.). The low molecular weight PAH are not persistent in organism tissues but are acutely toxic, whereas the higher molecular weight PAH may accumulate and persist in the tissues of some organisms, resulting in chronic toxicity. Some high molecular weight PAH are known to be mutagenic or carcinogenic.
- c. The PAH are metabolized by many aquatic animals, and certain metabolites may be responsible for carcinogenesis and other chronic effects. Since the parent compounds may not be found in tissues in significant concentrations following bioaccumulation tests, the feasibility of analyzing for metabolites needs to be considered.
- d. Sediments serve as a major reservoir for many of the PAH. These hydrophobic compounds have a high affinity for fine-grained sediments and organic matter, and thus can accumulate and persist in sediments, particularly those sediments typically found in maintenance dredging projects in the harbors of the industrial centers.
- e. Which compounds are selected must depend in part on the availability and ease of analytical methods. Specific recommendations included 16 PAH presently on the US Environmental Protection Agency (EPA) list of 129 "priority pollutants" (especially phenanthrene and its alkyl homologues) and dibenzothiophene, azaarenes, and nitroaromatics.
- f. In addition to analyzing sediment, or perhaps sediment pore water, acute and chronic effects on organisms need to be tested. The importance of assessing bioavailability was stressed. Photoinduced toxicity might be an additional consideration, and could be used as a bioassay technique.
- g. Quantitative structure-activity relationship (QSAR) techniques can assist in predicting toxicity and bioaccumulation potential from physical-chemical properties such as octanol-water partition coefficients (log P) and aqueous solubility.

### Format of the Workshop

9. All attendees were encouraged to participate in a plenary session held the evening of 12 May at the Holiday Inn, Vicksburg, Miss. This session centered around a buffet dinner and was intended to provide time for the participants to become acquainted with each other. During the dinner, each participant was asked to introduce him/herself to the group and to give a brief summary of his or her background and expertise.

10. The formal workshop sessions commenced Tuesday morning, 13 May, with a brief welcome address by Dr. Robert Whalin, Technical Director, WES. Dr. Richard Peddicord then presented an introduction and background to the problem of petroleum hydrocarbons in dredged material, as faced by the Corps Districts. The remainder of Tuesday was devoted to the environmental chemistry of petroleum hydrocarbons. Wednesday sessions focused on biological effects and QSAR, and Thursday morning concluded the workshop with refinement of a list of key hydrocarbon compounds generated by the prior discussions.

11. Each participant was asked to prepare a brief presentation on a general or specific aspect of environmental chemistry, biological effects, or QSAR of petroleum hydrocarbons. These presentations were given at appropriate times during the workshop sessions. The main objectives of the presentations were to introduce a given topic, to focus attention on the most important aspects of the topic, to give personal recommendations, and to stimulate subsequent discussions. The discussions were directed to ensure fulfillment of the primary purpose of the workshop.



## PART II: PROCEEDINGS OF THE WORKSHOP

### Introduction

12. Following the opening remarks by Dr. Whalin, Ms. Joan Clarke, the workshop chairperson, welcomed the participants and invited Dr. Richard Peddicord to provide a brief overview and historical perspective of the problem of petroleum hydrocarbons in dredged material. Dr. Peddicord noted that public laws (Section 103 of the Ocean Dumping Act and Section 404 of the Clean Water Act) regulating dredged material disposal focus on the biological effects rather than the mere presence or absence of contaminants. For example, ocean disposal of dredged material containing petroleum hydrocarbons as other than trace contaminants is prohibited. "Trace," however, is defined not in terms of chemical concentrations but only as that which is not sufficient to cause an effect. "Effect" refers to unacceptable adverse biological impact. Thus, the law requires an assessment of the potential effects of dredged material contaminants on biota, but does not necessitate chemical analysis to determine which contaminants are present in the dredged material or at what concentrations.

13. Regulatory perspectives were provided by Ms. Carol Coch, USAED, New York, and Mr. Jan Miller, USAED, Chicago. Ms. Coch stated that bulk sediment analyses have not proven to be reliable indicators of levels of petroleum hydrocarbons that are biologically available in sediments. As a result, biological evaluations such as bioassay/bioaccumulation tests are used for regulatory purposes. Based on these tests, the USAED, New York, has established "matrix values" for certain contaminants such as PCB. Matrix values were developed to prevent further degradation to the environment from dredged material disposal and were defined as the currently existing tissue concentrations. Since matrix values have not been established for petroleum hydrocarbons, the USAED, New York, has sought guidance from outside experts, by means of this workshop, on developing a reliable regulatory test for petroleum hydrocarbons that could be performed by contract laboratories.

14. In contrast to the evaluation approach used by the USAED, New York, Mr. Miller stated that the USAED, Chicago, and other regulatory agencies around the Great Lakes generally have accepted only bulk sediment chemistry as the means of evaluating disposal alternatives for contaminated dredged

material. Biological evaluations are beginning to be considered, and Dr. Michael Mac of the US Fish and Wildlife Service indicated that several such tests are in the research phase. He expects that they will be implemented in the future by Great Lakes regulatory agencies. Dr. Robert Engler reiterated that the purpose of developing these tests is for regulatory use, noting that the Districts need evaluation procedures based on cost-effective, routine analyses not requiring research levels of sophistication. He emphasized persistence, bioavailability, and toxicity (both acute and chronic) as important considerations in evaluating disposal alternatives.

15. One of the first problems facing Corps District regulators is which of the myriad petroleum hydrocarbon compounds to look for in sediment or in organism tissues. The group agreed from the start that analyses for all petroleum hydrocarbons would be impractical, prohibitively costly, and would not produce readily interpretable data. On the other hand, attempts at summary measures such as the oil and grease test are oversimplifications. Dr. Scott MacKnight referred to this test as meaningless "data taxation" because the results of the test are required under the Canadian Ocean Dumping Control Act permit process, but they cannot be interpreted. He found that results of the existing oil and grease test could not be correlated with concentrations of 16 PAH that were known to be important sediment contaminants. Furthermore, the mix of specific compounds, and therefore the potential biological effects, may be very different in two sediments having similar oil and grease values. Dr. Jim Petty concurred that gravimetric determination of oil and grease provides little information of any biological or ecological significance. Dr. Henry Tatem added that the oil and grease test can be misleading since it measures compounds that are not environmental contaminants.

16. Clearly, an intermediate approach is needed that avoids both the oversimplification of the oil and grease test and the uninterpretable complexity of attempts to analyze all petroleum hydrocarbons as individual compounds. As a first cut, Dr. Peddicord suggested that only certain classes of petroleum hydrocarbons may be important as dredged material contaminants, and asked for a consensus on which classes to consider. Before continuing with the response of the participants, however, it may be helpful at this point to clarify some pertinent terminology.

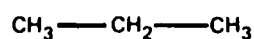
17. Hydrocarbons, by definition, are molecules composed only of carbon and hydrogen. Straight or branched chain hydrocarbons are called aliphatics; hydrocarbon ring structures are called cyclics. Hydrocarbons that contain only single bonds between adjacent carbon atoms are termed saturated (i.e., with hydrogen atoms); the presence of double or triple bonds makes them unsaturated. Reactivity of hydrocarbons generally increases with degree of unsaturation. Aromatics, in the classic sense, contain one or more six-carbon rings in which the carbon atoms are joined by alternating double and single bonds, e.g., benzene and naphthalene. Heterocyclics are ring structures that include elements other than carbon and hydrogen, such as nitrogen, sulfur, or oxygen. Cyclic hydrocarbons with side chains attached to a "parent" structure nucleus are alkylated. These structures are illustrated in Figure 1.

18. The workshop participants agreed that polycyclic (or polynuclear) aromatic hydrocarbons, i.e., those aromatics having two or more fused rings, are the most important class of hydrocarbon contaminants. A few participants suggested that some consideration might also be given to aliphatics and to interactions between hydrocarbons and other types of compounds.

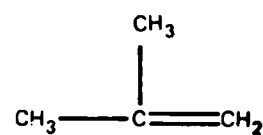
19. Several participants noted that the term "petroleum" is too restrictive because the source of the hydrocarbon contamination is not always known. Petroleum hydrocarbons originate only from petroleum products ranging from crude oil to highly refined products, and often contain heterocycles. Fuel oil spills and miscellaneous disposal (e.g., municipal surface runoff) are major sources of petroleum contamination to the aquatic environment. Mineralization of petroleum hydrocarbons and light, microbial or trace element catalyzed reactions result in *de novo* synthesis of many kinds of compounds. Hydrocarbons may also be biogenic or pyrogenic in origin. Biogenic hydrocarbons are produced by living organisms and consist primarily of aliphatics. Pyrogenic hydrocarbons are generated by combustion or incineration of various organic substances, including petroleum and coal and wood products, and enter aquatic systems mainly via atmospheric deposition and surface runoff.

20. In summary, the presence of hydrocarbons in sediment may be of concern regardless of source. The task of the workshop was now the selection of specific compounds within this broad family that would provide meaningful information for the regulatory evaluation of dredged material.

## ALIPHATIC



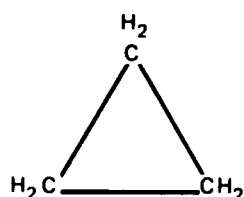
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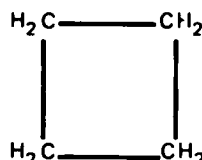
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UNSATURATED

## CYCLIC

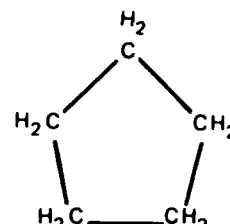
### 1) ALICYCLIC



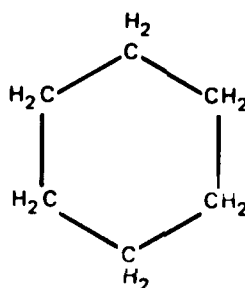
3-MEMBER  
RING



4-MEMBER  
RING

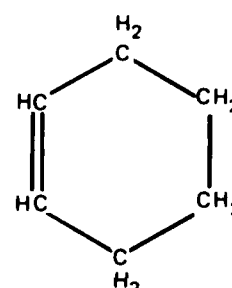


5-MEMBER  
RING



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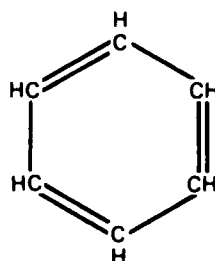
6-MEMBER RINGS



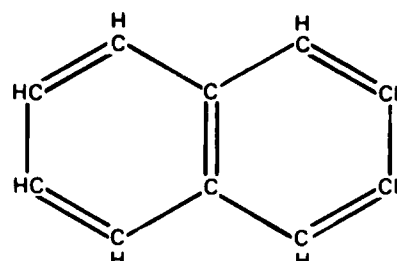
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6-MEMBER RINGS

### 2) AROMATIC

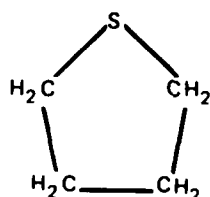


BENZENE

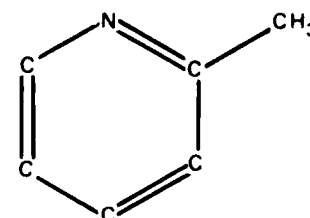


NAPHTHALENE

## HETEROCYCLIC



NONALKYLATED



ALKYLATED

Figure 1. Examples of basic hydrocarbon and heterocycle structures

## Technical Background

21. Each participant was asked to give a brief introduction to a general or specific aspect of the environmental chemistry and biological effects of hydrocarbon contaminants. These presentations were intended to provide background information for the selection of specific compounds and the development of a testing approach. Salient points of the introductions are summarized below.

### Environmental chemistry

22. Dr. Petty outlined the important aspects of environmental chemistry, including transport phenomena such as rain, runoff, and aerial deposition; fate, i.e., distribution through the ecosystem, including metabolic alteration and abiotic degradation; and bioavailability. He emphasized the importance of bioavailability in that if a compound is not taken up by organisms, it is not important as a contaminant. The disturbance caused by dredging may make contaminants more bioavailable. Dr. Petty suggested analyzing biota from the field as well as sediment. He listed the analytical techniques for enrichment and cleanup, separation, and detection of compounds in environmental samples. As a starting point for the selection of specific compounds, Dr. Petty recommended the alkylated hydrocarbons, heterocycles, and the "priority pollutant" PAH (Keith and Telliard 1979, Richards and Shieh 1986).

### Transport and partitioning

23. Dr. John McCarthy stated that a chemical entering an aquatic system can leave the system via volatilization, photolysis, or microbial mineralization. Within the system it can exist in a dissolved phase, or bound to dissolved organic matter, suspended particles, or sediment. The fate of a chemical is highly dependent upon its hydrophobicity and the reciprocal of its aqueous solubility. That is, binding and bioconcentration both increase as hydrophobicity increases and solubility decreases. Dissolved compounds will be more bioavailable than compounds bound to organic matter or sediment particles.

### Fate

24. Dr. MacKnight discussed the fate of hydrocarbons in aquatic systems. Input sources include runoff, discharges, atmospheric input, spillage, and dumping. After entry into water, hydrocarbons are subject to

biological uptake, biological or microbial alteration, photooxidation, volatilization, association with suspended particles, formation of particulates or tarballs, and settling of more dense material. Hydrocarbons entering sediments may leach into overlying waters, be taken up or altered by organisms, be chemically or microbiologically degraded within the sediment, or be oxidized in intertidal sediments. These processes over time result in a qualitative shift to simpler compounds and a quantitative shift to lower concentrations of the remaining compounds.

#### Abiotic degradation

25. Degradation of hydrocarbons in aquatic systems, according to Dr. Lee Wolfe, occurs primarily through biological and chemical oxidation reactions in the water column. Chemical oxidation reactions include both thermochemical and photochemical processes. The PAH generally will not undergo abiotic reduction reactions, although some heterocycles will. Redox reactions will not occur with chemicals bound to sediments; the chemicals must desorb into the water column first. Dr. Wolfe stressed that hydrocarbons are fairly unreactive abiotically.

#### Microbial degradation

26. The PAH must undergo metabolism to reactive metabolites in order to exhibit their mutagenic or carcinogenic properties, according to Mr. Michael Heitkamp. Eukaryotic organisms utilize monooxygenases to initially attack PAH to form arene oxides, followed by the enzymatic addition of water to form *trans*-dihydrodiols. In contrast, prokaryotic organisms metabolize PAH by an initial dioxygenase attack, forming *cis*-dihydrodiols that are further oxidized to dihydroxy products, which are precursors to ring-opening reactions. The rate of degradation of PAH is inversely related to the number of fused benzene rings, and degradation half-lives are very long for the high molecular weight PAH. Alkylated PAH occur commonly in petroleum hydrocarbons, and alkylation also depresses microbial degradation dramatically relative to unsubstituted PAH, since alkyl groups inhibit metabolic systems from attacking the fused rings. Dr. Richard Lee mentioned that microbes apparently do not readily degrade PAH having five or more rings, whereas many animals rapidly metabolize both small and larger compounds. Dr. Robert Lipnick said that long or branched aliphatics also slow down microbial degradation. Mr. Heitkamp summarized by stating that steric hindrance slows metabolic attack on compounds;

i.e., the more the rings are shielded from attack by their steric configuration, the longer the degradation half-life.

#### Bioavailability

27. Dr. Joseph O'Connor defined bioavailability as the extent to which a contaminant can move from an environmental source into the tissues of organisms. Since there is no known mechanism for active transport from source to biota, it must be assumed that partitioning is the mechanism. The PAH body burden is difficult to measure because alteration is induced in the organism, and the original compounds observed in the sediments may not be present in tissues. Thus, it would be necessary to look for metabolites or remnants of parent compounds. Dr. Lee and Dr. Peter Landrum mentioned bivalves and certain amphipods as exceptions in that they appear to have limited ability to degrade PAH. Dr. Lee, however, added a caveat concerning the use of bivalves as reliable indicators of hydrocarbon bioavailability because of these organisms' natural cyclic variability in uptake of all kinds of compounds. Dr. Stratford Kay commented that this cyclic variability may be true of most organisms, regardless of their ability to metabolize PAH. Dr. O'Connor surmised that the potential for predicting bioavailability rests with physical and chemical properties and the development of QSAR. Dr. Lipnick agreed that QSAR predictions of uptake in fish hold well for the lower molecular weight compounds. Mr. Vic McFarland stated, however, that physical-chemical based estimation procedures may work less well with PAH than with other compounds such as PCB because the PAH are subject to multiple degradative processes.

#### Biological effects

28. In an overview of biological effects, Dr. Tom Dillon focused on the exposure-response relationship. Response can be measured at many levels of increasing biological complexity from atomic or molecular to community or ecosystem. The mechanistic explanation of an observed response can be found at a lower level, while its biological or ecological importance is found at higher levels. As biological organization increases, the ecological relevance of a response also increases, whereas the response sensitivity generally decreases. Conversely, biochemical evaluations may be quite sensitive, but the ecological significance of the observed response may be difficult to interpret. From the perspective of environmental protection, it is populations and communities, rather than individual organisms, that are of major concern. However, from a practical standpoint, it is difficult to evaluate

sublethal contaminant-related effects at the population or community level of biological organization, especially in a predictive mode. Consequently, most sublethal bioassessment evaluative methodologies are conducted at the next lower level of biological organization, the whole organism.

29. In aquatic toxicology, water concentration and sediment concentration, rather than "dose," are used as exposure concentrations, since dose technically refers to an internally administered concentration. Environmental exposure controls the dose and, thus, the response. The actual dose is best reflected by the tissue concentration. Dr. O'Connor objected that for metabolized compounds, the water concentration is closer to the true dose than the tissue concentration, due to metabolic breakdown of the parent compound. Drs. Dillon and O'Connor agreed that for regulatory purposes, the focus is on response and there may be no need to know the dose as long as generally accepted evaluative tests are available.

30. Dr. Lee stated that in considering environmental protection at the community level, reproduction is the response of primary importance. Dr. Landrum added that growth is also an important community-level response, since reduced growth could remove a species from a commercially viable resource even if the numbers of individuals were not affected. Dr. Dillon indicated that survival, reproduction, and growth are the end points selected by WES as best suited for regulatory evaluations. Survival tests (bioassays) are commonly done, but dredged material is rarely acutely toxic. Survival and reproduction can be summarized as a single demographic statistic, the intrinsic rate of population increase ( $r$ ). This population statistic is attractive from a regulatory standpoint because it can be evaluated in a variety of aquatic organisms and it has relatively straightforward numerical interpretability (i.e., positive values of  $r$  reflect increasing population growth, whereas negative values indicate a population in decline).

#### Toxicology

31. According to Dr. Landrum, the most important hydrocarbons from a general toxicological standpoint are the aliphatics, aromatics, and phenols. Their toxicity, however, may be mitigated in aquatic systems. The phenols, for example, generally contribute little to sediment contamination because they are readily metabolized and are relatively water soluble. Among the aliphatics, acute toxicity (measured as LC50) decreases as the size of the molecule increases. The LC50 for many of the larger molecules occurs at



levels approaching their maximum possible concentration in water (i.e., at a high percent of saturation). If aliphatics are present in sediment in high enough quantities, they could pose a problem, although generally they would end up as tarballs and not cause direct toxicity to organisms. In moderate sediment concentrations, aliphatics would not be expected to be toxic. Monoaromatics are acutely toxic at a low percent of saturation but are relatively water soluble and volatile, and thus unlikely to accumulate to critical levels in sediment. The higher molecular weight PAH are acutely toxic only at concentrations approaching saturation; however, important chronic effects occur at much lower concentrations. Low levels of PAH can alter or inhibit the development of embryos from aquatic organisms. Furthermore, PAH have been implicated in the production of cancer in fish both in the field and in the laboratory.

32. Dr. Landrum mentioned that photoinduced toxicity of PAH may become an important factor when contaminated sediments are disturbed by dredging or in shallow aquatic environments. Many aquatic invertebrates and larval fish are virtually transparent. If these organisms swim through suspended sediment near the bottom, receive a dose of contaminants, and move to the surface where they become exposed to sunlight, they may be killed rapidly from a low internal level of PAH. In juvenile fish, the mechanism of photoinduced toxic action occurs at the gill surfaces, resulting in degradation of the gill membranes (Oris and Giesy 1985). Photoinduced toxicity has been attributed to many of the PAH and other compounds as well (Kagan et al. 1983, 1985; Pengerud et al. 1984; Landrum et al., in press). Dr. Landrum speculated that photoinduced toxicity could be developed as a useful screening tool for sediment toxicity, although most of the workshop participants agreed that more research would be required to develop this into a standardized test for regulatory purposes.

33. Dr. Kay commented that most areas in which dredged material disposal would occur would probably be quite turbid, due to suspended particulates. Very little light would penetrate more than a few centimeters. Thus, photoinduced toxicity would likely present a problem only in the case of disposal in very clear water. The phenomenon would more likely be observed in clear-water laboratory systems. However, this would not diminish the utility of photoinduced toxicity as a potential screening procedure for toxic PAH in sediments.

### Biochemistry and physiology

34. Some PAH are metabolized rapidly by aquatic animals to increase water solubility and enable the animal to eliminate these compounds, according to Dr. Lee. Metabolism occurs mainly in the liver, and to some extent in the gills and gut, through oxidation followed by conjugation processes. Reactive electrophiles produced in the metabolic process are toxic, though transitory. Metabolism of PAH is accelerated in organisms with a history of exposure to PAH or other chemical contaminants that induce hepatic mixed-function oxidase (MFO) enzymes.

35. Oxidation of PAH occurs via the MFO enzyme system. The MFO system also regulates some aspects of lipid metabolism and the metabolism of steroid (reproductive) hormones. Some PAH and metabolites may therefore interfere with sexual maturation by affecting hormone synthesis, catabolism, or function. Dr. Lee noted that MFO systems are less active in invertebrates than in vertebrates, especially mammals, whereas conjugating systems are much more active in invertebrates.

### Metabolism

36. Dr. John Stein further described the metabolic pathways in aquatic organisms. PAH are metabolized by the MFO enzyme system to epoxides, which can rearrange to phenols and dihydrodiols. The formation of dihydrodiols is catalyzed by the enzyme epoxide hydrolase, whereas formation of phenols occurs nonenzymatically. These primary metabolites are then either detoxified by conjugating enzymes to form conjugates that are more easily excreted, or further activated by the MFO enzyme system. The resulting reactive metabolites can bind to biological macromolecules; binding to DNA may result in genotoxic effects, including induction of tumors. The "bay region" (Figure 2) of angular PAH is a critical metabolic site. Many PAH having a molecular configuration that includes bay regions are carcinogenic, the ultimate carcinogen being a bay-region dihydrodiol epoxide. Dr. Stein stated that cause-and-effect relationships have not been definitively established between contaminants in the field and prevalences of neoplasms in exposed aquatic organisms. However, studies by Malins and coworkers have shown that the prevalences of liver lesions in fish are positively correlated with the presence of PAH in sediment (Malins et al. 1984).

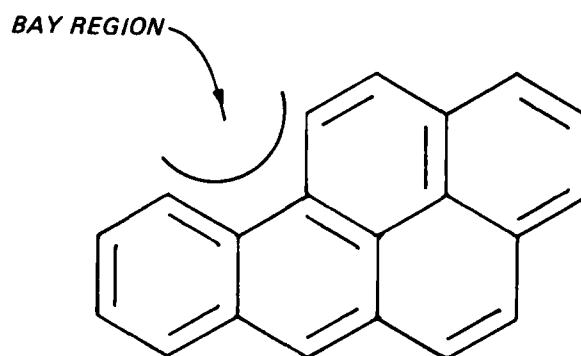


Figure 2. Bay region of benzo(a)pyrene

Quantitative structure-  
activity relationships (QSAR)

37. The QSAR, according to Dr. Lipnick, are a set of methodologies by which physical or chemical properties of compounds, or other molecular descriptors, can be used to derive mathematical models incorporating biological data based upon well-defined end points, such as 96-hr LC50. Such a QSAR model is generally developed for a single biological species using chemicals that have a common molecular mechanism of action. The data used to develop a QSAR model are considered a "training set." The resulting model can then be used to quantitatively predict toxicity for untested chemicals that are considered to act by the same mechanism as the training set. Dr. Lipnick mentioned several mechanisms of action at increasing levels of complexity (Table 1). Most organic nonelectrolytes, such as PAH, exhibit physical-type acute toxicity or narcosis action (Level 1). For these compounds, the 96-hr LC50s may be predicted accurately by octanol/water partition coefficients ( $\log P$ ) up to  $\log P$  of 4.5 or greater as the duration of the exposure increases. However, predicted toxicities for many compounds will exceed their aqueous solubilities; such compounds will be limited in their ability to elicit acute toxicity to aquatic organisms under equilibrium conditions. Surfactants and certain other compounds act by a membrane-destructive mechanism (Level 2), which does not apply to PAH. Synergists (Level 3) consist of chelating agents, surfactants, enzyme inducers, and enzyme blockers.

38. Level 4 toxicity is an electrophile mechanism resulting from irreversible binding to critical nucleophilic sites on enzymes and other biological target molecules such as DNA. In the Level 5 proelectrophile

Table 1  
Mechanisms of Toxicity of Industrial Chemicals

<u>Level of Complexity</u>	<u>Mechanism Type</u>
1	Physical/baseline (narcosis)
2	Membrane destructive
3	Synergist
4	Electrophile
5	Proelectrophile
6	Pharmacophore
7	Propharmacophore

mechanism, nonelectrophilic compounds are metabolized to electrophiles, and toxicity then occurs as with Level 4. This is one mechanism of carcinogenesis. Molecules such as the anticholinesterase agent paraoxon, which bind to a biological receptor, may be classified as pharmacophores (Level 6); malathion, which requires prior metabolic activation for this purpose, may be classified as a propharmacophore (Level 7). The PAH are not expected to act by either of these mechanisms.

39. The acute aquatic toxicity of PAH in general can be attributed to the narcosis mechanism. Other biological responses may result from more complex mechanisms, such as Level 4 and Level 5, but QSAR has been applied only to a limited extent to quantitatively model such effects.

#### Consensus Recommendations of the Workshop

##### Recommended compounds

40. Aliphatics. Some consideration was given to the analysis of aliphatic hydrocarbons in regulatory evaluations. However, the consensus was reached that aliphatics should not be included for a number of reasons. First, aliphatics usually will not cause toxicity in aquatic systems, since most aliphatics will end up as tarballs and may not have direct toxicity. Dr. Lee concurred that crude oil high in aliphatics will not be very toxic, and long-term effects of crude oil spills are minimal. Also, Dr. Landrum

indicated that aliphatics will have no effect on organisms in the aquatic environment because high-percent saturations are required to produce toxicity. Furthermore, Dr. Dillon mentioned that aliphatics are readily degraded by microorganisms, relative to aromatics. Second, Mr. McFarland suggested that any acute toxicity problems, whether attributable to aliphatics or to any other compounds or interactive effects, will be detected by acute toxicity tests. Third, determination of aliphatics poses analytical problems. Dr. Lipnick indicated that aliphatic toxicity in the laboratory can be predicted by QSAR, but that many aliphatic isomers are too hard to identify using current analytical techniques. In analytical chemistry procedures, according to Mr. McFarland and Drs. Stein and Petty, the aliphatic fractions are routinely discarded and not reported, or are reported only as total aliphatics or Fraction 1 (F1).

41. Aromatics. The workshop participants agreed that the aromatics, especially the PAH, are important, particularly in terms of chronic toxicity. According to Dr. Lipnick, all PAH exhibit baseline (Level 1) toxicity, although Drs. O'Connor and Lee pointed out that not all PAH are readily bioavailable and most do not attain concentrations in water that are acutely toxic. Concern over the PAH as environmental pollutants stems from the acute toxicity of two- and three-ring compounds, such as naphthalene and phenanthrene, and chronic toxicity of the higher molecular weight compounds, particularly as manifested in carcinogenicity.

42. Several alternatives for analysis of PAH were explored. First, Dr. MacKnight asked if one or two or possibly a limited number of PAH among the large number of hydrocarbons could be used in a regulatory review scenario in a manner analogous to the role played by PCB for the organohalogenes. Dr. Lee replied that regulators could focus on certain compounds such as fluoranthene, which is common in most petroleum products. However, the general feeling was that the PAH are too diverse in their environmental behavior and potential effects to be adequately represented by only one or two compounds.

43. Dr. Peddicord then asked if it would be informative to distinguish classes of PAH based on structural, analytical, biological, or other similarities, as for example, log P groups or ring classes. Dr. Lipnick assented, in that the percent composition of a mixture in terms of log P can be determined using reverse phase liquid chromatography. Mr. McFarland raised the objection

that bioavailability of PAH is not necessarily correlated with log P. Physical-chemical properties such as log P interact in highly complex relationships with the gross composition of compartments of the environment, and with the biology and behavior of organisms. Organic carbon content of the sediments, trophic transfer, and migrant behavior are examples of properties or processes that limit the usefulness of simple classifications of PAH based only on log P or other single properties. Concerning ring classes, Dr. Wolfe stated that capillary gas chromatography separates compounds based on molecular weight and can be used to fractionate by ring number at relatively low cost. However, Dr. Petty objected that this technique does not work that well in practice because all the compounds do not separate well, and thus the resulting quantitative values for ring classes could be widely varying estimates. Dr. Landrum also pointed out the lack of analytical standards for ring classes.

44. Dr. Petty recommended instead that analysis be done for the 16 priority pollutant PAH (Figure 3). Such analyses would be somewhat less expensive than analysis for ring classes and would require less technical expertise in the laboratory. The analytical results would also have better interpretability than ring classes. Dr. Wolfe agreed that quantitation of the 16 priority pollutant PAH would be a relatively simple analytical procedure. He added that the priority pollutant list was derived from water surveys, in which these compounds were the most frequently occurring and the easiest to analyze. Dr. Petty stated that the 16 priority pollutants are widely accepted as such and thus have sociological value, which makes them appealing for regulatory use.

45. All participants agreed that the 16 priority pollutant PAH should be submitted as the primary components of the list to be recommended for regulatory evaluation of hydrocarbons in dredged material. Discussions then centered on whether additions or deletions should be made to the list. Several classes of compounds were considered to be of toxicological importance in addition to the PAH. However, the group agreed that further research was needed on biological effects and on the development of analytical techniques before specific compounds could be added to the list. The contaminant classes of potential concern are discussed in the section entitled "Research recommendations."

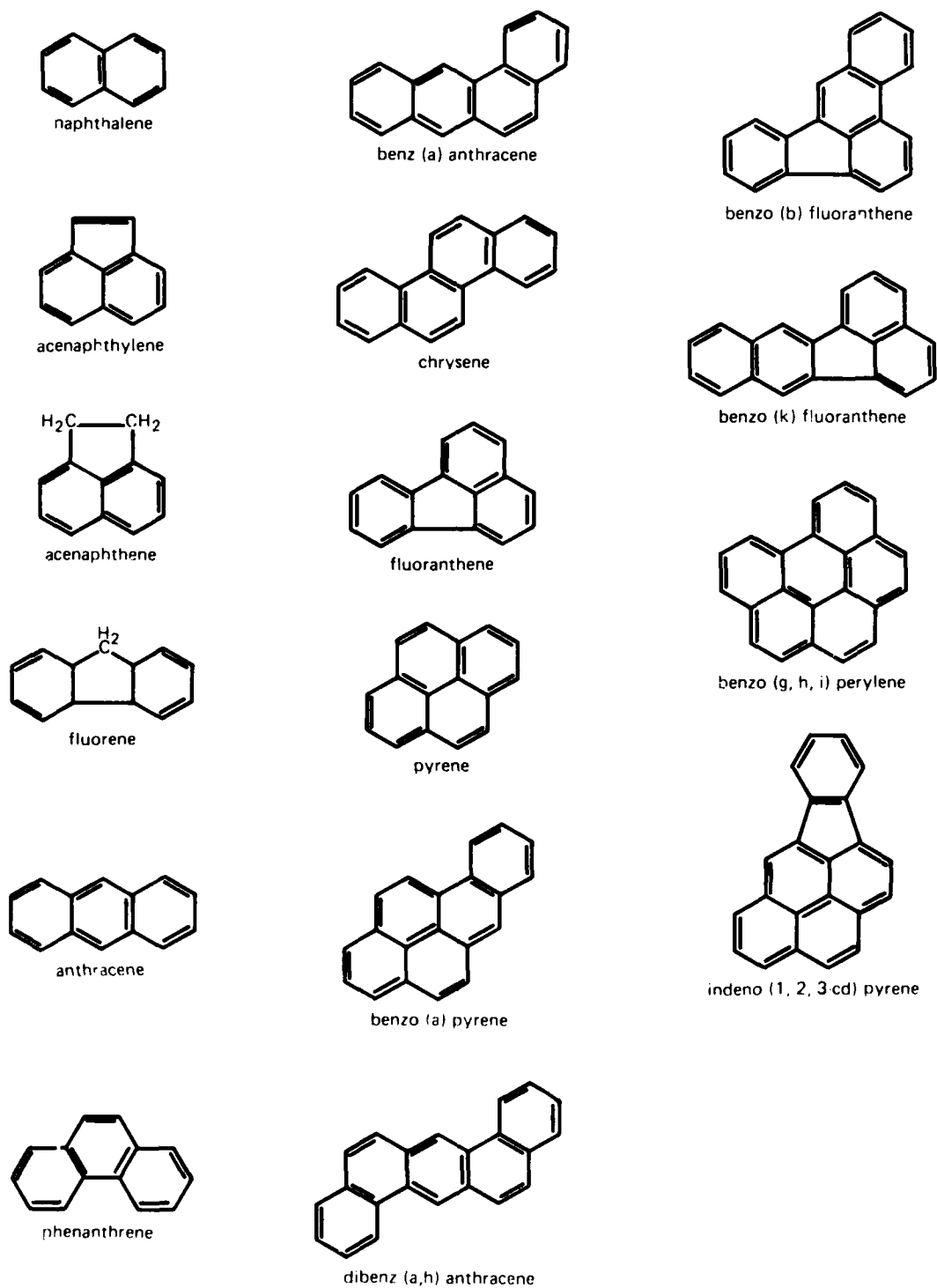


Figure 3. Structures of the 16 priority pollutant PAH

46. The utility of several PAH on the priority pollutant list for dredged material evaluations was questioned on biological and analytical grounds. Mr. Heitkamp reported that naphthalene is relatively water soluble and so volatile that an accurate value is difficult to obtain by analytical procedures. He claimed that any toxicity due to naphthalene would be covered by an acute toxicity test, and recommended dropping naphthalene from the list. Dr. Lee stated that there are similar analytical problems with acenaphthene and acenaphthylene, but Dr. Petty countered that the problems are not as severe as with naphthalene. Mr. Heitkamp questioned whether both benzo(b)-fluoranthene and benzo(k)fluoranthene should be retained on the list. Dr. Lee responded that these two compounds separate well in high-performance liquid chromatography analysis. Dr. O'Connor recommended keeping both since they are easy to analyze and say something about transport. Dr. Lee stated that he has never seen benzo(g,h,i)perylene reported from environmental samples, and in general he would not expect six-ring compounds to be bioavailable. However, Dr. Stein indicated that his colleagues have seen uptake of six-ring PAH. Dr. Kay also reported substantial levels of benzo(g,h,i)perylene in harbor sediments and some exposed organisms. The consensus of the group was to drop naphthalene and retain the remaining 15 priority pollutant PAH on the list of PAH compounds recommended for regulatory analyses of dredged material. The behavior, fate, and effects of these 15 were considered by the group to be fairly representative of hydrocarbons that are known in general to have biological effects.

#### The testing approach

47. Tiered testing. The concept of basing regulatory evaluations on a tiered testing scheme was proposed early in the workshop, and a suggested approach gradually took shape during the ensuing sessions. Mr. McFarland and Dr. MacKnight initially recommended a tiered approach using less expensive tests as first-tier screens. Dr. Engler mentioned that the first test is a "reason to believe" test that the sediment is contaminated, and proposed looking at toxicity followed by identification of contaminants. Dr. Peddicord pointed out that the ocean disposal regulations require both toxicity and bioaccumulation tests.

48. Several alternatives were proposed as the first testing tier in a hierarchical approach. Dr. Lipnick stated that acute toxicity is clearly related to log P, and thus a log P screen could be used as the initial test.



Mr. Heitkamp proposed using organic extracts in mutagenicity tests (such as the Ames test or other genotoxicity test) as the first screen, but Dr. O'Connor pointed out analytical limitations to using this procedure with PAH. In addition, Dr. John Stegeman stated that some compounds from sediment extracts may be highly toxic to bacteria. Dr. Kay suggested that a total PAH value could be used as a screen by comparison with cutoff values. However, the group felt that a total PAH value may give little indication of toxicity or bioavailability, and that this approach might be no less expensive but would certainly provide less information than simply analyzing for specific compounds such as the priority pollutant PAH.

49. Group sentiment gradually moved in favor of using toxicity tests as a first testing tier. Acute toxicity tests with the crustaceans *Daphnia* in fresh water and *Mysidopsis* in salt water are commonly done, have standard accepted procedures, and the results are easy to interpret. Consensus was reached to suggest a two-tiered testing approach proposed by Dr. McCarthy. The first tier of tests would comprise both an acute toxicity test and sediment analysis for the 15 priority pollutant PAH. If results of this tier indicate concern over PAH, then the second tier would be conducted. This would consist of a 10-day bioaccumulation test to demonstrate bioavailability. The actual criteria for triggering the second tier of tests would be a regional authority decision (e.g., by Corps District regulators). In most situations, both testing tiers would probably be conducted. However, if acute toxicity is seen in the first tier, a decision might be reached to impose disposal restrictions without conducting further tests. Conversely, if first-tier tests indicate no acute toxicity and negligible levels of sediment contaminants, the decision might be that bioaccumulation tests are not necessary.

50. Dr. Lee stressed the need to pick bioaccumulation indicator species carefully. Many organisms metabolize PAH rapidly, and the parent compounds would not be found in their tissues after a 10-day uptake study. Filtering bivalves and some species of amphipods are two groups that appear to have a limited ability to metabolize PAH. However, he cautioned that it is necessary to have a good understanding of the species used because filtering bivalves take up and discharge contaminants continuously, and may not provide a good reflection of contaminant levels in the water or sediment. Dr. Stegeman noted also that bivalves exposed to noxious conditions can close up and remain closed for weeks. Dr. MacKnight recommended using the filter-feeding clam

*Mercenaria*, and Dr. Tatem suggested using an active deposit-feeding bivalve, *Yoldia*, as well. Dr. Landrum recommended the amphipod *Pontoporeia* for the Great Lakes region. Consensus was reached to propose the use of *Mercenaria*, or a suitable substitute depending on salinity and geographical region, in the 10-day bioaccumulation tier of the testing approach. Dr. Stegeman mentioned that background samples are essential to determine the levels of any contaminants present in the tissues of the study organisms prior to the bioaccumulation testing.

51. Some discussion centered on the problem of metabolites, and the possibility of analyzing tissues for metabolites rather than parent compounds. Dr. Lee contended that analyzing for metabolites is difficult; Drs. Stein and Petty agreed that such analysis would be too costly, because there are too many metabolites (many of which are still unknown) and the analytical procedures are not well defined. Dr. Lee labeled analysis of metabolites as "sublime," meaning that it would be appropriate for research but is currently impractical for regulatory use. Ms. Coch noted that regulatory programs often depend upon the use of contract laboratories that may not be well equipped to perform other than routine analytical procedures.

52. Regulatory problems and perspectives. Mr. Miller of the USAED, Chicago, stated his understanding that acute toxicity testing is the most direct and straightforward analysis for the lower molecular weight PAH, whereas bioavailability analysis is needed for the bigger molecules. He predicted a move toward more bioassessment by regulatory agencies in the Great Lakes region, and expected that biologically based interpretations can gradually be worked into the regulatory process.

53. Ms. Coch inquired whether the acute toxicity and bioaccumulation tests could be performed without the sediment analysis. She felt that the biological testing could provide adequate information about the potential of a sediment for adverse environmental impact, without the added expense of bulk sediment analysis. Dr. Petty said that, without the sediment analysis, there would be no information on what PAH are present in the sediment, and Dr. Lee added that they would be unable to determine any relationship between sediment contaminant levels and organism tissue residues. Ms. Coch pointed out that harbor sediments are extremely heterogeneous, and the District has found no correlation between sediment contaminant levels and tissue residues. Dr. MacKnight argued that the bioavailability test is just as susceptible to

heterogeneity problems, and Dr. Stein suggested analyzing the same sediment that is used in the bioaccumulation study, rather than some other sediment. Dr. McCarthy reiterated that District regulators can better interpret bioaccumulation data if they know what is in the sediment. Dr. O'Connor mentioned that it would be impossible to do quality control on the bioaccumulation tests without knowing contaminant levels in the sediment. Dr. Peddicord pointed out that it may be sufficient for regulatory purposes to compare bioaccumulation from the dredged material to bioaccumulation from a reference sediment. The relationship between actual levels of contaminants in the dredged material and tissue concentrations in exposed organisms may be of interest but of lesser importance.

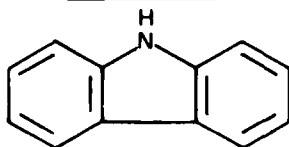
54. Quality assurance/quality control (QA/QC). Dr. Petty stressed the critical need for QA/QC, particularly when testing is done by contract laboratories. He cited a situation in which Columbia National Fisheries Research Laboratory (CNFRL) issued a Request for Proposals requiring that performance samples spiked by CNFRL be analyzed and the results submitted along with the proposals. Few analytical laboratories were found to perform well. Dr. Petty recommended using QA/QC techniques such as split samples, spiked samples, and blind replicates. He said that contracting laboratories should be required to submit QC results, along with detailed written specifications of the analytical procedures employed. Dr. MacKnight mentioned that the USEPA was now preparing five marine sediment (Chesapeake Bay) materials as QA/QC of trace organics in sediments, specifically including the 15 PAH of interest. He added that the National Research Council of Canada will soon be making available as reference materials four PAH in marine sediments.

#### Research recommendations

55. All workshop participants agreed that analysis for the 15 selected priority pollutant PAH in sediments and in organism tissues is sufficiently standardized, reliable, and informative to be suitable for regulatory use. Other classes of hydrocarbons or petroleum derivatives are likely to have environmental significance as well. However, knowledge of their occurrence and biological effects and the development of analytical techniques have not progressed to the point at which any of these compounds can be promoted for routine use in regulatory evaluations. The workshop participants did name several classes of environmentally important hydrocarbons and gave specific examples of compounds in these classes (Figure 4), with the recommendation

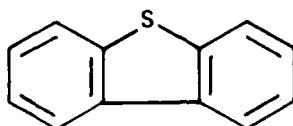
## HETEROCYCLES

### NITROGEN



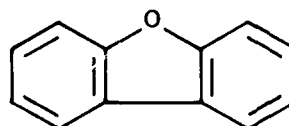
carbazole

### SULFUR

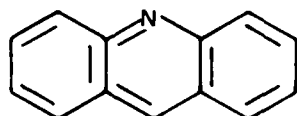


dibenzothiophene

### OXYGEN

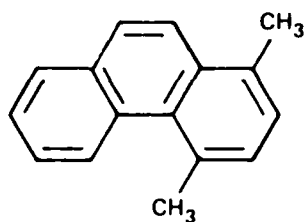


dibenzofuran



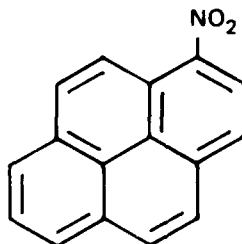
acridine

### ALKYLATED POLYCYCLIC AROMATICS



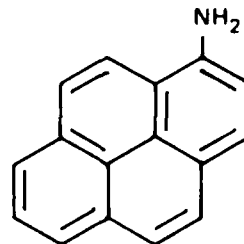
1,4 - dimethylphenanthrene

### NITRO- AROMATICS

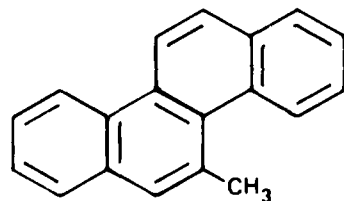


1 - nitropyrene

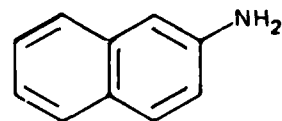
### AROMATIC AMINES



1 - aminopyrene



5 - methylchrysene



2 - naphthylamine

Figure 4. Classes of hydrocarbons and example compounds recommended for further research

that further research be conducted. Some of the examples given are commonly found in sediments and are suspected of having carcinogenic or genotoxic effects.

56. Perceived research needs include: (a) compilation of lists of hydrocarbons that have been found in sediments around the country, so that researchers know what is routinely present or absent, (b) selection of representative compounds for research and eventual regulatory use, (c) development of reliable, standardized analytical methodologies; and (d) development of standardized tests to assess bioavailability of PAH and their biological effects such as carcinogenicity, reproductive toxicity, genotoxicity, and photoinduced toxicity.

### PART III: SUMMARY OF MAJOR AGREEMENTS

57. A consensus was reached by the workshop participants on the following points:

- a. The oil and grease test does not provide a meaningful summary measure of hydrocarbon contamination in sediment. At the other extreme, analyses for all petroleum hydrocarbons as individual compounds would be too difficult, costly, and uninterpretable. An intermediate approach is needed for regulatory evaluation.
- b. "Petroleum" is too restrictive a term, and any hydrocarbon contamination of dredged material should be considered, regardless of source of the hydrocarbons.
- c. Aliphatic hydrocarbons need not be included in regulatory evaluations because they may pose analytical difficulties and generally do not cause major environmental impacts in the context of dredging and disposal.
- d. Polycyclic aromatic hydrocarbons (PAH) are the most important class of hydrocarbon contaminants in dredged material due to their toxicity and persistence.
- e. Analysis for a limited number of specific PAH would have better interpretability than analyses for ring classes or groups based on log P ranges.
- f. The list of compounds recommended for regulatory evaluation of hydrocarbons in dredged material includes the following 15 priority pollutant PAH:
  - (1) Acenaphthene.
  - (2) Acenaphthylene.
  - (3) Anthracene.
  - (4) Benz(a)anthracene.
  - (5) Benzo(a)pyrene.
  - (6) Benzo(b)fluoranthene.
  - (7) Benzo(g,h,i)perylene.
  - (8) Benzo(k)fluoranthene.
  - (9) Chrysene.
  - (10) Dibenz(a,h)anthracene.
  - (11) Fluoranthene.
  - (12) Fluorene.
  - (13) Indeno(1,2,3-cd)pyrene.
  - (14) Phenanthrene.
  - (15) Pyrene.

Naphthalene, which is also considered a priority pollutant PAH, has not been included in this list because it is too volatile to give accurate analytical results and too water soluble to persist in sediments. It was felt that a high level of naphthalene would be manifested as mortality in acute toxicity tests.

- g. A tiered testing approach to regulatory evaluations of PAH in dredged material was recommended. This would begin with a general assessment of the likelihood of contamination. The first testing tier would include an acute toxicity test and analysis of the sediment for the 15 priority pollutant PAH. The second-tier test would consist of a 10-day bioaccumulation test to demonstrate bioavailability.
- h. In assessing the potential for bioaccumulation, organisms that have limited or no ability to metabolize PAH should be used. Analysis of tissues for unmetabolized parent compounds is thus simplified. The group suggested the clam *Mercenaria* or a suitable substitute bivalve, or an amphipod such as *Pontoporeia*, as appropriate species to use in the 10-day bioaccumulation test.
- i. The group recommended against analysis for metabolites of PAH in a routine regulatory program until more research is completed and analytical methods are better established.
- j. A critical need is QA/QC evaluations and procedures, especially when a variety of laboratories are used by a regulatory agency for testing and review purposes.
- k. Recommendations for future research focus on the development of analytical procedures and biological testing protocol for the evaluation of alkylated PAH, and of representative hydrocarbons and derivatives from classes other than the PAH. These include the N-, S-, and O-containing heterocycles (particularly the acridines and thiophenes), nitroaromatics, and aromatic amines.
- l. Biological tests that need to be refined and standardized include assays for carcinogenicity, genotoxicity, reproductive effects, and photoinduced toxicity.

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## APPENDIX A: SCOPE OF WORK\*

### Regulatory Identification of Petroleum Hydrocarbons in Dredged Material

for

US Army Engineer District, New York

#### Background

1. Concerns about possible environmental impacts of dredging and dredged material disposal are often based, at least in part, on the likely presence of petroleum hydrocarbons in the sediment. Regulatory analyses of dredged material and/or tissues of animals exposed to it have often included quantification of total oil and grease or total petroleum hydrocarbons in response to this concern. Scientific advances over the last several years have made this degree of analytical sophistication increasingly inadequate, either to accurately assess the potential for environmental impact or to allay concerns expressed by the public or other agencies. Literally hundreds of the individual compounds known collectively as petroleum hydrocarbons have been identified in sediment, water, and tissue samples. The complex variety of compounds which make up petroleum hydrocarbons span a wide range of water solubility, persistence, bioavailability, toxicity, bioaccumulation potential, carcinogenicity, and overall biological importance. The environmental significance of any specific sample is determined by the particular mix of compounds which make it up. For this reason "summary" type analyses, such as total oil and grease or total petroleum hydrocarbons, cannot provide sufficient information to accurately evaluate the potential for environmental impact of petroleum-contaminated samples. Two samples with the same total petroleum hydrocarbon content can often be of vastly different environmental concern when one consists largely of compounds of relatively low bioavailability, persistence, toxicity, and overall biological importance, and the other has important quantities of bioavailable, persistent, toxic, bioaccumulative, and/or carcinogenic compounds.

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\* Prepared by Environmental Laboratory, US Army Engineer Waterways Experiment Station, Vicksburg, Miss.

2. Clearly the "summary" type analyses are inadequate for regulatory purposes, and more precise and interpretable analyses are needed. However, it is equally clear that exhaustive analyses of all petroleum compounds present would be far too time consuming and costly and would produce an unwieldy volume of data for regulatory purposes. What is needed is to simplify the complexity that is petroleum hydrocarbons by focusing on clearly identified key compounds or classes of compounds which are of most importance environmentally. In this manner, adequate resolution for defensible evaluations could be obtained at a time and cost that are practical in the dredged material regulatory program.

3. The public, state, and other Federal agencies are placing increasing emphasis on petroleum hydrocarbon evaluations. Not all these activities are scientifically sound, and most do not consider the economic and administrative factors important to the Corps of Engineers' regulation of dredged material. The Corps' interest and public image would be well served by development of a technically sound and practically implementable approach to regulatory evaluation of petroleum hydrocarbons in dredged material.

#### Objectives

4. In a letter of 15 Feb 85 to Dr. Richard Peddicord of the WES, Mr. James Mansky of the USAED, New York (NYD), requested assistance in identifying particular components of the complex petroleum hydrocarbon mixture that are most appropriate for analysis as a basis for environmental regulation of dredged material. The proposed work will accomplish this objective based on chemical, physical, and biological considerations such as solubility, degradability, bioavailability, association with sediments, availability of analytical techniques, bioaccumulation potential, persistence in tissues, toxicity, carcinogenicity, and overall environmental importance. Identification of the key petroleum components will also provide a basis for development of guidance for environmental interpretation of petroleum hydrocarbon concentrations in the dredged material regulatory program.

### Approach

5. Past experience has proven that the most productive way to arrive at consensus findings in complex scientific areas is through a technical working group of experts. Therefore, a group of widely recognized authorities with extensive expertise in environmental impacts of petroleum hydrocarbons in sediments will be identified. After careful consideration, approximately 10 will be selected to participate. This group will include scientists from government, academia, and the private sector who have a knowledge of dredging, disposal, and the dredged material regulatory process. A representative of NYD will be included, and the District will be consulted in the identification of other participants. Those chosen will be provided a statement of goals and objectives, and will be asked to produce a written description of their perceptions and suggestions and to be prepared to elaborate and justify their inputs at the workshop. This premeeting work will help form the basis of the final agenda as well as maximize the amount of valuable workshop time that can be devoted to productive interactive discussion. At the conclusion of the working group meeting, the WES will seek a consensus from the participants concerning which petroleum hydrocarbon components are appropriate for analysis in the dredged material regulatory program. The WES will then prepare a report in the form of a WES Miscellaneous Paper summarizing the working group goals, activities, conclusions, and recommendations. The report will be supported not only by the expertise of the participants but also by justification provided by participants from the scientific literature for specific conclusions.

6. The USAED, Chicago, has also contacted the WES seeking technical assistance in similar areas concerning regulatory evaluations of petroleum hydrocarbons in sediment. Because of the similarities in the two requests, complementary responses have been prepared. A separate Scope of Work is being submitted to the Chicago District for development of state-of-the-practice scientific interpretation of potential environmental impacts of petroleum hydrocarbon components identified in this Scope. Although this Scope is not dependent upon the work proposed to the Chicago District, results of that work should be of great interest and relevance to NYD. Therefore, we propose that both sponsors be provided information copies of all documents prepared for the other. Each District would pay for one Scope and have its objectives fully

met by receiving full benefit of both efforts. This provides an unusual opportunity for very timely and cost-effective mutual benefit on an important environmental matter. It is possible that the Chicago District may decide not to fund the work proposed to it, in which case the efforts in this Scope of Work would stand on their own.

#### Product

7. A report will be prepared describing the study objective, methods, findings, and conclusions. Conclusions will be supported on the basis of the consensus of the recognized authorities participating, and selected documentation from the scientific literature. A complete draft report will be submitted to the NYD for review and comment prior to preparation of the final report. The final report will be published as a WES Miscellaneous Paper. Sufficient copies will be published for limited distribution of the WES reports as well as 100 copies to be supplied to the NYD.

### Schedule

<u>Event</u>	<u>Accomplished by</u>
1. Agreement on scope and receipt of funding by the WES	1 Nov 85
2. Selection of participants in conjunction with NYD	1 Dec 85
3. Receipt of preworkshop input from each participant	1 Mar 86
4. Finalize commitment for participants to attend meeting	1 Apr 86
5. Distribution of premeeting information	1 Apr 86
6. Workshop conducted at WES	12 May 86
7. Draft report to NYD and participants for review	1 Sep 86
8. Comments from reviewers received at WES	1 Oct 86
9. Final report to NYD for approval for publication	2 months after event 8 is accomplished
10. Final approval from NYD for publication received at the WES	1 month after event 9 is accomplished
11. Published report distributed	3 months after event 10 is accomplished

Regulatory Interpretation of Petroleum Hydrocarbons  
in Dredged Material

for  
US Army Engineer District, Chicago

Background

8. Concerns about possible environmental impacts dredging and dredged material disposal are often based, at least in part, on the likely presence of petroleum hydrocarbons in the sediment. Regulatory analyses of dredged material and/or tissues of animals exposed to it have often included quantification of total oil and grease or total petroleum hydrocarbons in response to this concern. Scientific advances over the last several years have made this degree of analytical sophistication increasingly inadequate, either to accurately assess the potential for environmental impact or to allay concerns expressed by the public or other agencies. Literally hundreds of the individual compounds known collectively as petroleum hydrocarbons have been identified in sediment, water, and tissue samples. The complex variety of compounds which make up petroleum hydrocarbons span a wide range of water solubility, persistence, bioavailability, toxicity, bioaccumulation potential, carcinogenicity, and overall biological importance. The environmental significance of any specific sample is determined by the particular mix of compounds which make it up. For this reason "summary" type analyses, such as total oil and grease or total petroleum hydrocarbons, cannot provide sufficient information to accurately evaluate the potential for environmental impact of petroleum-contaminated samples. Two samples with the same total petroleum hydrocarbon content can often be of vastly different environmental concern when one consists largely of compounds of relatively low bioavailability, persistence, toxicity, and overall biological importance, and the other has important quantities of bioavailable, persistent, toxic, bioaccumulative, and/or carcinogenic compounds.

9. Clearly the summary type analyses are inadequate for regulatory purposes, and more precise and interpretable analyses are needed. However, it is equally clear that exhaustive analyses of all petroleum compounds present would be far too time consuming and costly and would produce an unwieldy

volume of data for regulatory purposes. What is needed is to simplify the complexity that is petroleum hydrocarbons by focusing on clearly identified key compounds, or classes of compounds, which are of the most importance environmentally. In this manner, adequate resolution for defensible evaluations could be obtained at a time and cost that are practical in the dredged material regulatory program.

10. The public, state, and other Federal agencies are placing increasing emphasis on petroleum hydrocarbon evaluations. Not all these activities are scientifically sound, and most do not consider the economic and administrative factors important to the Corps of Engineers' regulation of dredged material. The Corps' interest and public image would be well served by development of a technically sound and practically implementable approach to regulatory evaluation of petroleum hydrocarbons in dredged material.

11. In a letter of 8 May 85 to the attention of Dr. Richard Peddicord at the WES, the Chicago District's Commander and Director requested assistance to Mr. Jan Miller in advancing the technical approach to regulatory evaluation of petroleum hydrocarbons in dredged material. Need for assistance was identified in the following general areas: (a) identifying a manageable number of key components of the petroleum hydrocarbon mixture that are most appropriate for regulatory purposes, (b) development of guidance on environmental evaluation of particular levels of these components in sediments which may be dredged, and (c) assessment of dredging and disposal in Great Lakes harbors in light of (a) and (b).

#### Objectives

12. The proposed work will address the first two of the aforementioned areas of interest and will provide (a) identification of the particular components of the complex petroleum hydrocarbon mixture that are most appropriate for analysis as a basis for regulatory evaluation of sediments proposed for dredging, and (b) guidance on state-of-the-practice scientific interpretation of potential environmental impacts of the petroleum hydrocarbon components identified in objective (a).

### Approach

13. Past experience has proven that the most productive way to arrive at consensus findings in complex scientific areas is through a technical working group of experts. Therefore, a group of 8 to 12 widely recognized authorities with extensive expertise in environmental impacts of petroleum hydrocarbons in sediments will be identified. Those selected will be carefully chosen to include scientists from government, academia, and the private sector who have knowledge of dredging, disposal, and the dredged material regulatory process. A representative of the Chicago District will be included, and the District will be consulted in the identification of other participants. Those chosen will be provided a statement of goals and objectives, and will be asked to produce a written description of their perceptions and suggestions and to be prepared to elaborate and justify their inputs at the workshop. This premeeting work will help form the basis of the final agenda as well as maximize the amount of valuable workshop time that can be devoted to productive interactive discussion. At the conclusion of the working group meeting, the WES will seek a consensus from the participants concerning the objectives of the meeting. The WES will then prepare a report in the form of a WES Miscellaneous Paper summarizing the working group goals, activities, conclusions, and recommendations. The report will be supported not only by the expertise of the participants but also by justification provided by participants from the scientific literature for specific conclusions.

14. The USAED, New York (NYD), has also contacted the WES seeking technical assistance in similar areas concerning regulatory evaluation of petroleum hydrocarbons in sediment. Because of the similarities in the two requests, complementary responses have been prepared. A separate Scope of Work is being submitted to NYD for funding which will accomplish the first objective stated above for this Chicago work. We propose that the Chicago District benefit from the work conducted for the NYD during FY 86 and receive that report, and that the NYD benefit from and receive the report on the work conducted during FY 87 for the Chicago District. The first of the Chicago District's objectives as stated above would be met by the NYD-sponsored work, and the second objective would be met by the work sponsored by the Chicago District. Likewise, the NYD would also receive the full information and



report sponsored by the Chicago District. Each District would pay for one Scope and have its objectives fully met by receiving full benefit of both efforts. This provides an unusual opportunity for very timely and cost-effective mutual benefit on an important environmental matter.

15. It is important to point out that work on the second Chicago objective cannot be initiated until the first has been accomplished. Therefore, achieving both objectives hereby proposed to the Chicago District is dependent upon the work proposed to the NYD. If for some reason the NYD should decide not to fund the work proposed to it, we would suggest the work therein be supported by the Chicago District to achieve its first objective. In that case, the information and report would go only to the Chicago District. Support of the work contained in this scope to meet the Chicago District's second objective would become the subject of future discussions.

#### Product

16. A report will be prepared describing the study objective, methods, findings, and conclusions. Conclusions will be supported on the basis of the consensus of the recognized authorities participating, and selected documentation from the scientific literature. A complete draft report will be submitted to the Chicago District for review and comment prior to preparation of the final report. The final report will be published as a WES Miscellaneous Paper. Sufficient copies will be published for limited distribution of WES reports, as well as 100 copies to be supplied to the Chicago District.

### Schedule

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APPENDIX B: PREWORKSHOP INPUTS FROM  
TECHNICAL PARTICIPANTS

TOXICOLOGICAL ASPECTS OF PETROLEUM HYDROCARBONS  
IN DREDGED MATERIAL

William H. Benson, Ph.D.\*

Adel H. Karara, Ph.D.\*

The purpose of this workshop is to identify key petroleum hydrocarbons which will be of most use in evaluating dredged material samples. Petroleum hydrocarbons may be categorized into five major classes: phenols, monoaromatics, polycyclic aromatics, aromatic amines and thiophenes. Because of their potential to cause chronic toxicological effects we have focused our attention on the polycyclic aromatic hydrocarbons (PAHs). Although this class of petroleum hydrocarbons has a low water solubility, the PAHs are persistent in the environment due to slow microbial degradation. In addition, the PAHs, in general, have a high potential for bioaccumulation. In mammals, the acute toxicity of orally administered PAHs is expected to be low because they are generally poorly absorbed from the gastrointestinal tract. However, because of their favorable partition coefficient properties, some PAHs are easily absorbed percutaneously and systemic effects have been observed. For example, dimethyl benzanthracene showed acute lethal effects when applied topically to the skin and when injected interaperitoneally (Cancer Research Supp. (2), 1955). We have summarized a general review of selected PAHs in the following table.

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SUMMARY OF TOXICOLOGICAL ASPECTS OF SELECTED  
POLYCYCLIC AROMATIC HYDROCARBONS

Compound	Presence in Sediment <sup>a</sup>	Acute toxicity <sup>b</sup>		Carcinogenicity <sup>b,c</sup>
		Fish	Mammals	
Naphthalene	High	Moderate	High	
2-Methylnaphthalene	Moderate	NA <sup>d</sup>	Low	
Anthracene	Moderate	NA	Low	
Phenanthrene	High	NA	Moderate	+
Chrysene	High	NA	Moderate	+
Pyrene	High	NA	Low	
Fluorene	High	NA	NA	
Fluoranthene	High	NA	Low	
Benzo[e]pyrene	High	NA	Moderate	+
Benzo[a]pyrene	Moderate	NA	Moderate	+

PRINCIPAL MOLECULAR TYPES OF ADDITIONAL POLYCYCLIC AROMATIC HYDROCARBONS  
WHICH HAVE PRODUCED TUMORS IN MICE BY REPEATED TOPICAL APPLICATION<sup>c</sup>

1:2 Benzanthracene and derivatives  
 1:2, 5:6 Dibenzanthracene and derivatives  
 1:2, 3:4 Dibenzanthracene  
 9,10 - dimethyl - 1:2, 7:8 dibenzanthracene  
 3:4 Benzphenanthrene and derivatives  
 1:2, 3:4 and 1:2, 5:6 dibenzophenanthrene  
 3:4 Benzpyrene  
 1:2, 3:4 dibenzpyrene and 3:4, 8:9 dibenzpyrene  
 Cholanthrene and derivatives

<sup>a</sup> Malins et al. (1985) JNCI 74(2), 487.

<sup>b</sup> Registry of Toxic Effect of Chemical Substances (1977).

<sup>c</sup> Gerarde (1960) Toxicology and Biochemistry of Aromatic Hydrocarbons

<sup>d</sup> Not available.

Evaluation of Polycyclic Aromatic Hydrocarbons in Sediments:  
Environmental and Microbiological Factors  
Affecting Their Biodegradation\*

There is considerable concern about the fate of petroleum hydrocarbons in the environment since many of these compounds are toxic and some have been shown to be potent mutagens and carcinogens. An environmental risk assessment of sediments containing petroleum hydrocarbons requires information on their occurrence, toxicity, metabolism, biological activity, bioavailability, and persistence in the environment. However, such risk assessments are complicated by the fact that crude oils are complex mixes of aliphatic, alicyclic and aromatic hydrocarbons, often containing nitrogen or sulfur, which vary in their toxicological and chemical properties. At the National Center for Toxicological Research, we have utilized microbial, mammalian, and environmental test systems to investigate the kinetics and metabolic pathways for the bioactivation, detoxification and degradation of an important fraction of petroleum hydrocarbons, the polycyclic aromatic hydrocarbons (PAHs).

PAHs are discharged into aquatic ecosystems from combustion processes involving fossil fuels or by natural means such as oil seeps, petroleum spills, or in run-off from forest and prairie fires. Due to their hydrophobic nature, most PAHs in aquatic ecosystems are associated with sediments where they may become buried and persist until resuspension or removal by dredging. Toxicological concern for some of the smaller molecular weight PAHs such as benzene and naphthalene and their methylated derivatives is primarily for their acute toxicity to environmental organisms. For example, naphthalene and some of its derivatives such as 1- or 2-methylnaphthalene are some of the most toxic, water-soluble components of crude oils. As the molecular size of the PAHs increases up to 4 or 5 fused benzene rings, their lipophilicity and persistence in the environment greatly increases and toxicological concern shifts towards chronic toxicity, primarily carcinogenesis. It is generally accepted that PAHs must undergo metabolic activation to exhibit their mutagenic or carcinogenic properties. Extensive studies on the bioactivation of PAHs have documented the formation of unstable arene oxides which are capable of binding to cellular macromolecules, an event proposed to initiate their carcinogenic effects. This bioactivation of PAHs can be enhanced or hindered by the presence of various chemical substituents at certain positions on the aromatic nucleus. For example, a methyl substituted PAH, 7,12-dimethylbenz[a]anthracene, has greater mutagenicity and carcinogenicity than the parent compound, benz[a]anthracene.

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\* Mr. Michael A. Heitkamp, National Center for Toxicological Research, Food and Drug Administration, Jefferson, AR 72079.

Although much is known concerning the degradation and bioactivation or detoxification of PAHs by pure cultures of microorganisms and mammalian enzyme systems, far less is known about the rate and chemical pathway of PAH metabolism in natural ecosystems. Since the expression of acute and chronic toxicity by PAHs in natural ecosystems is determined by both the concentration and duration of their exposure to environmental organisms, differences in environmental half-lives among ecosystems may produce profound differences in environmental toxicity. Furthermore, the degradation of PAHs in the environment can be affected by several natural factors which may differ among ecosystems, such as organic and inorganic nutrient levels, temperature, previous chemical exposure, microbial adaptations and oxygen tension. In addition, many species of bacteria and fungi coexist in natural ecosystems and may act independently or in concert to metabolize aromatic hydrocarbons. Recognition of the complexity of natural ecosystems has resulted in the use of environmental microcosms as controlled models which simulate selected components and processes in the environment. Microcosms are useful for providing information concerning the potential toxicological impact of PAHs in natural ecosystems.

In the laboratory of Dr. Carl E. Cerniglia at the National Center for Toxicological Research, we have utilized multi-component microcosms containing natural sediment and water to determine rates for the environmental degradation of some representative PAHs containing from 2 to 5 fused aromatic rings. We have found that differences in the physical, chemical and microbial characteristics of ecosystems can greatly affect the disposition and persistence of PAHs in the environment. The half-lives for the degradation of PAHs varies significantly among ecosystems and is related to the aromatic ring size and microbial adaptations which occur after chronic exposure to either anthropogenic or petrogenic chemicals. We are now investigating the physiological, enzymatic and genetic characteristics of these adapted microbial populations. Furthermore, we have determined the metabolic pathway and stereochemistry of initial oxidation reactions for some PAHs in environmental microcosms. These studies have confirmed the occurrence and predominance of prokaryotic metabolic pathways for the degradation of PAHs in natural ecosystems and have enabled the isolation and identification of some key chemical intermediates occurring during the complete mineralization of PAHs. Such microcosm studies designed to compare predictions of PAH biodegradation from pure or mixed culture studies to actual degradation in natural systems are necessary to determine how accurately data can be extrapolated for risk assessments from in vitro experiments to aquatic and terrestrial ecosystems.

Since petroleum hydrocarbons typically contain many different PAHs, environmental monitoring protocols for dredged sediments as well as biodegradation and toxicity evaluations must utilize representative PAHs. The selection of representative PAHs must be based upon consideration of their known occurrence in sediments, availability and ease of chemical methodologies for their detection, toxicity to environmental organisms, chemical and physical characteristics, potential for bioaccumulation into foodchains resulting in human exposure, genotoxicity and persistence in natural ecosystems. Although the number of PAHs selected for monitoring must be constrained due to the time, effort and expense of chemical analyses, hopefully, these considerations will ensure the selection of PAHs of the greatest environmental concern. PAHs also occur commonly in coke oven emissions, coal tar and used motor oils, all of which may also contaminate the environment. Concern for PAHs from these sources in dredged sediments may require the selection of additional PAHs for monitoring.

## Sediment Hydrocarbon Workshop Preliminary Ideas\*

Since petroleum products consist of complex mixtures of two major classes of compounds, aliphatic hydrocarbons and aromatic hydrocarbons, it is unlikely that the use of just a few compounds as specific markers will be sufficient for setting criteria. While both classes of compounds are toxic in sufficiently high concentrations, the aromatic fraction appears to be more persistent and to produce a greater range of toxic responses. Further, since the mixtures in sediments are likely to represent a wide range of commercial products and compositions, the approach for setting criteria must be able to respond to these changes. A tiered approach seems to be the most appropriate to minimize the amount of testing that must be performed and to permit rapid decision making where possible. While it would be nice to have a scheme that would provide criteria defining a particular sediment as non-toxic with a simple test, such schemes do not exist.

The tiered approach will likely incorporate both bioassays and chemical analyses. The overall approach should be one to set levels where the easiest tests, both chemical and biological, could be used to define a sediment as toxic. In the realm of bioassays, a sediment bioassay such as that described by Swartz et al. 1985 employing amphipods should provide a sufficiently sensitive assay for acutely toxic sediments. One might also test the sediment pore water with such tests as the seven-day Mount-Norberg Ceriodaphnia reproduction test. This test should be more sensitive and assay a different end point. One additional test might prove to be extremely useful and that is a phototoxicity test. This makes use of the photoinduced toxicity of polycyclic aromatic hydrocarbons. Daphnia could be exposed to sediment pore water under low-level light or gold fluorescent light for 24 to 48 h. The animals would then be exposed in clean water to either sunlight or to a laboratory light source that reproduces the sunlight spectra including the ultraviolet portion. If the animals have accumulated sufficient phototoxic polycyclic aromatic hydrocarbons, they will succumb quickly and an  $LT_{50}$  could be determined. This might prove to be a sensitive test for PAH and other phototoxic compounds where the sediment pore water is not acutely toxic. A similar test might be performed with a

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\* Dr. Peter Landrum, Great Lakes Environmental Laboratory, 2300 Washtenaw Ave., Ann Arbor, MI 48104-4590.



benthic organism provided the organism could stand being exposed to light after accumulating compounds from sediment. After these simple acute bioassays, chronic bioassays examining reproduction, survival or growth of benthic organisms, oligochaetes or amphipods, could be useful indicators of effects. This would also be the time to determine bioavailability with bioconcentration studies.

Coupled to the above bioassays would be a tiered set of chemical analyses. The first assays would be the simplest, probably total petroleum or perhaps total aliphatic and total aromatic hydrocarbons. These assays with a positive bioassay would be sufficient to define the sediment as toxic. Further chemical analyses of defined groups of compounds such as the polycyclic aromatic hydrocarbons and/or their heterocyclic homologs combined with the results of the chronic studies would serve to screen sediments for lower level contamination. An index of combinations of amounts of aliphatic, aromatic and specific levels of effects in bioassay would define cutoffs for describing the toxicity of a sediment. It may be useful to even describe the hazard of a sediment based on bioconcentration factors of specific compounds combined with chemical analyses yielding concentrations in the sediments above cutoff levels of specific compounds. The absence of effects at this level in the bioassays and very low concentrations in the sediments should be sufficient to place the sediment in a category that could be considered non-toxic or having a minimal level of hazard.

PETROLEUM HYDROCARBONS OF USE IN  
ANALYSIS OF DREDGED MATERIALS\*

The monoaromatics, e.g. benzene, toluene, are perhaps the most acutely toxic of the petroleum fractions. However, because of their volatility the monoaromatics are absent or at low concentrations in most sediments. Thus, for dredged material the focus should be on polynuclear aromatic hydrocarbons (PAH). The PAH are an important fraction of petroleum and petroleum products and some have toxic, as well as carcinogenic and mutagenic, properties. Much information can be derived from an analysis of PAH in dredged material. A high proportion of alkylated PAH are associated with petroleum. PAH produced from high temperature processes, e.g. fuel combustion, are largely non-alkylated. Thus, analysis of dredged material for a particular aromatic hydrocarbon and its alkylated homologs, e.g. phenanthrene, should be useful in understanding the source of the PAH. In addition to analysis of substituted and non-substituted PAH there should be analysis of PAH with known mutagenic and carcinogenic properties. Examples include benzo(a)pyrene, benzo(k)fluoranthene, benzo(b)fluoranthene, and methyl chrysenes. Microbial degradation of these 4 or 5-ringed PAH is relatively slow and they would be expected to persist in dredged materials.

Another advantage of a focus on PAH is the extensive work that has been done on these compounds in sediments. The procedures for analysis have been described using gas-liquid chromatography, high-performance liquid chromatography, and mass spectroscopy.

It would also be useful to analyze for minor components of petroleum which are known to have biological effects, such as azaarenes. The azaarenes, as well as nitroaromatics, have been found in sediments and would likely occur in dredged materials. These compounds are only at low concentrations in petroleum but can be produced during combustion of petroleum or petroleum products and carried on particles in the air to coastal sediments.

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# DISCUSSION PAPER ON QUANTITATIVE STRUCTURE-ACTIVITY RELATIONSHIPS\*

## Bioaccumulation

The partitioning behavior of nonelectrolyte organic compounds from water to aquatic organisms has been demonstrated (ref. 1) to correlate with the log P parameter, where P is the partition coefficient between n-octanol and water (eq. 1).

$$\begin{array}{lcl} \log \text{BCF} = & 0.79 \log P - 0.40 & (1) \\ (n=122) & (r^2=0.86) & \end{array}$$

Nine of the compounds for which bioconcentration data were used to derive eq. 1 are hydrocarbons. The comparison between measured and predicted bioconcentration factors in freshwater fishes for these compounds is shown in Table 1. In general, there is good agreement between the experimental and predicted values. The hydrocarbons span a log P range of 3.16-4.86 and a molecular weight range of 92-192. It would be desirable to obtain bioconcentration data on other hydrocarbons of higher log P and higher molecular weight to validate this model for compounds of this type. Hawker and Connell (ref. 2) have derived pharmacokinetic models for predicting time to achieve 99% bioconcentration equilibrium (eq. 2) and 1% of this value (eq. 3) for nonelectrolyte organic compounds as a function of log P,

$$\log t_{eq} = 0.663 \log P - 0.284 \quad (2)$$

$$\log t_s = 0.663 \log P - 2.947 \quad (3)$$

where  $t_{eq}$  and  $t_s$  are the times in days to reach 99% and 1% equilibrium between the fish and water. These models support the need for longer bioconcentration tests to adequately assess of the potential hazard of such very hydrophobic compounds (ref. 3).

## Aquatic Toxicity

The correlation of the bioconcentration in fish of simple nonreactive nonelectrolytes such as hydrocarbons is also reflected in a correlation of log P with aquatic toxicity. Those compounds which act solely by a Meyer-Overton mechanism are postulated to exhibit intrinsic toxicity at the same molar concentration at the site of action within the organism (ref. 4). Könnemann (ref. 5) derived a QSAR (eq. 4) for the toxicity to guppies a series of such organic compounds, where the LC50 is in micromoles/L.

$$\begin{array}{lcl} \log (1/\text{LC50}) = & 0.0871 \log P - 4.87 & (4) \\ (n=50) & (r=0.988) \quad S=0.237 & \end{array}$$

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Table 1. Comparison of Measured and Predicted Bioconcentration Factors of Hydrocarbons in Fish

No.	Chemical Name	M.W.	Log P <sup>a</sup>	Bioconcentration Factor			Species	Tissue	Time	Ref. <sup>d</sup>
				Meas. <sup>b</sup>	Cal.					
1.	Napthalene	128.17	3.59	427	27.		Fathead	W. body	28D	1
				79	273		Coho salmon	Muscle	35D	17
2.	Biphenyl	154.20	4.09	1318	678		Rainbow trout	Muscle	4D	1
3.	2-Methylphenanthrene	192.26	4.86	3020	2750		Fathead	W. body	4D	1
4.	Fluorene	166.22	4.38	1288	1148		Fathead	W. body	28D	1
5.	Phenanthrene	178.23	4.46	2630	1329		Fathead	W. body	4D	1
6.	2-Methylnapthalene	142.20	3.84	191	430		Coho salmon	Muscle	35D	17
7.	1-Methylnapthalene	142.20	3.84	129	430		Coho salmon	Muscle	35D	17
8.	Toluene	92.14	3.16	91	125		Fathead	W. body	32D	1
9.	Acenaphthene	154.21	3.92	389	498		Bluegill	W. body	28D	8

a.) Log P values as reported in G.D. Veith and P. Kosian (1982).

b.) Reported as log RCF.

c.) From eq. 1.

d.) Ref. numbers as cited in G.D. and P. Kosian (1982).

Similar Meyer-Overton QSAR models have been reported for other fish species derived from test data on additional compounds (ref. 6,7,). In Table 2, a comparison is provided between the measured and predicted LC50 values for hydrocarbons reported by both K $\ddot{o}$ nnemann (ref. 5) and Geiger et al. (ref. 8). In general, the QSAR predictions agree within a factor of 2 of the measured values. Only the data for cyclohexane appear as an outlier. K $\ddot{o}$ nnemann attributed this anomalous result to rapid metabolism of cyclohexane by the fish. Using additional data on hydrocarbons, Lipnick and Dunn (ref. 7) provided evidence that K $\ddot{o}$ nnemann's result was more likely an experimental artifact of testing a chemical having high volatility from water in a static test.

The toxicity of simple nonelectrolyte compounds acting solely by a narcosis or Meyer-Overton mechanism may be water solubility limited. Water solubility can be estimated from log P and melting point using eq. 5 (ref. 9),

$$\log S = 7.3 - 1.12 \log P - 0.017 MP \quad (5)$$

where S is the water solubility in micromoles/L, and MP is the melting point in °C (for liquid solutes, a nominal value of 25°C is used). If equations 4 and 5 are solved simultaneously by setting log LC50 and log S equal, this yields a log P value of 8.05. Therefore, liquid solutes whose log P values are less than eight are predicted to show narcotic toxicity at levels predicted by eq. 4, in experiments of sufficient duration to reach equilibrium. Hydrocarbons and other nonelectrolytes with melting points exceeding 25°C will exhibit a solubility cutoff at lower log P values. For example, anthracene and phenanthrene are isomers each having calculated log P (ref. 10) values of 4.49. Both have predicted LC50 values of 1.6 mg/L. However, their melting points are markedly different, with anthracene, 216°, and phenanthrene, 100° (ref. 11). Based upon these melting points, water solubilities of 0.66 mg/L for phenanthrene and 0.0071 mg/L for anthracene are predicted (eq. 5). The predicted toxicity for anthracene exceeds its predicted solubility by about two orders of magnitude, and toxicity is not expected to be observed experimentally based solely upon a narcosis mechanism. For phenanthrene, the values are similar, and toxicity may be observed. The difference in melting point, relative solubility, and toxicity between these two isomers reflects the higher degree of symmetry of anthracene with a corresponding increase in the stability of its crystal lattice (ref. 12). Nevertheless, while the acute toxicity of hydrocarbons such as anthracene may be water solubility limited when tested individually, this may not be the case if such a substance is a component of a mixture, as the toxicity of mixtures of compounds acting solely by a narcosis mechanism is additive (refs. 13-15). In addition, the mixed melting points of such solutes are almost always markedly depressed below those of the pure crystalline materials (ref. 12), resulting in increased solubility compared to the pure solutes.

Table 2. Comparison of QSAR Predictions with Fish LC50 Data for Hydrocarbons

No.	Chemical	M.W.	Log P	Ref. <sup>a</sup>	LC50 (mg/L)		Species	Time
					Meas.	QSAR Pred. <sup>b</sup>		
1.	Benzene	78.11	2.13 <sup>c</sup>	1	6.35	80.8	Guppy	14 D
2.	Toluene	92.14	2.59 <sup>c</sup>	1	68.3	37.9	Guppy	14 D
3.	m-Xylene	106.17	3.09 <sup>c</sup>	1	37.7	16.0	Guppy	14 D
4.	o-Xylene	106.17	3.09 <sup>c</sup>	1	35.2	16.0	Guppy	7 D
5.	p-Xylene	106.17	3.09 <sup>c</sup>	1	35.2	16.0	Guppy	7 D
6.	Cyclohexane	84.16	3.18 <sup>c</sup>	1	>168	10.6	Guppy	7 D
7.	Napthalene	128.17	3.32 <sup>d</sup>	2	6.14	12.19	Fathead	4 D
8.	1,9-Decadiene	138.25	4.90 <sup>d</sup>	2	0.29	0.55	Fathead	4 D
9.	Acenaphthene	154.21	4.07 <sup>d</sup>	2	1.73	3.25	Fathead	4 D
10.	tert-Butylstyrene	160.26	4.84 <sup>d</sup>	2	0.495	0.723	Fathead	4 D

a.) H. Konemann (1981); D.L. Geiger, et al. (1985).

b.) Equation 2.

c.) Log P values reported in Ref. 1.

d.) Log P values calculated using the CLOGP 3.3 computer program.

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## Hydrocarbons in Dredged Sediments\*

The purpose of the discussion is to evaluate a method(s) that can be used to assess the impact of hydrocarbons in sediment proposed for dredging and (potentially) open-water disposal. The present initial method of evaluation centres around the "oil and grease" test. This test follows from work in the 1960's and 1970's on the evaluation of oil refinery aqueous effluents and the procedures were carried over (with some modifications) to analysis of petroleum hydrocarbons in sediments.

The London Dumping Convention and subsequent national legislation has defined the components of interest as "crude oil, fuel oil, heavy diesel oil, and lubricating oils, hydraulic fluids and any mixtures containing any of them" and placed these components in Schedule I: Prohibited Substances. Two questions can be raised:

- 1) Should we only consider those petroleum hydrocarbons which correspond to the above?
- 2) Should we consider that the Convention was attempting to indicate a concern for materials containing a large proportion of aromatic hydrocarbons and that therefore the method of evaluation should centre on aromatic compounds and not all petroleum hydrocarbons?

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Work in our laboratory has indicated that the "oil and grease" test is not measuring many of the aromatic compounds and may in fact not be measuring many of the aliphatic hydrocarbons either; that is, it may only be considering a narrow window of compounds which may be present.

The Convention has also emphasized petroleum products without considering that many of the same hydrocarbons can originate in sediment from coking oven effluents, deposition of waste ash or deposition of waste wood combustion/treatment products. We have observed that the oil and grease test is relatively non-responsive to complex PAH from sediment near a coking oven. Two questions can be raised:

- 1) Should we only consider petroleum hydrocarbons and ignore complex hydrocarbons from other sources which are known to be toxic and/or carcinogenic?
- 2) Should the Convention be re-defined to be compound (or group of compounds) specific for this category as it has for other contaminants of concern, and not define the category on the basis of a few broad groups of products?

Over the past ten years, we have seen significant advances in the ability to determine trace metal and various individual trace organic compounds in marine sediments to low detection limits and good precision/accuracy of analysis. The "oil and grease" test in comparison is very out-dated and basically a waste of the project proponent's

money. On the other hand, the high cost of using GC/MS to determine all of the petroleum hydrocarbons in complex harbour sediments forces the proponent back to the "oil and grease" test. Two questions can be raised:

- 1) Can we develop a technique that will provide the regulatory agency with sufficient information to assess the degree of impact? For example, would using HPLC to separate aromatic hydrocarbons into ring classes provide sufficient detail for the toxicologist to estimate toxicity or sub-lethal effects?
- 2) Should the method(s) of analysis only consider certain groups or classes of hydrocarbons and ignore others?

Throughout any discussion, we should focus on two points of view:

- 1) The regulatory agency wants the proponent to "define the nature of the material to be disposed"; i.e., indicate the impact of disposal.
- 2) The proponent wants to obtain regulatory approval to dredge and dispose of the sediment by defining the material, but not at such a cost or effort as to overwhelm the budget of the actual dredging.

Regulatory Identification of Petroleum Hydrocarbons  
in Dredged Materials\*

The U.S. Army Corps of Engineers needs to simplify analyses of petroleum hydrocarbons by focusing on clearly identified key compounds or classes of compounds which are of the greatest importance environmentally. The problem can be considered at two levels of effect endpoints:

- a. compounds which can produce acute toxicity in exposed organisms; and
- b. compounds which are not acutely toxic, but which can accumulate in organisms. These compounds may result in long-term adverse effects, such as reduced fecundity or tumor formation, or may raise environmental concern in terms of a potential for accumulation in foodchains leading to humans.

The water solubility (conversely, the hydrophobicity) of the compound limits the potential for acute toxicity. Very hydrophobic compounds are not, in general, acutely toxic because their limited solubility prevents aqueous concentrations from reaching levels that would cause immediate toxic response. Concern about acute effects should, therefore, be focused on relatively low molecular weight compounds, such as the two- and possibly three-ring polycyclic aromatic hydrocarbons (PAH) such as naphthalene and methylnaphthalene.

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The higher molecular weight compounds are more hydrophobic, less water soluble, and have a much greater potential for binding to sediment and for biological accumulation in organisms. The affinity of compounds for binding to sediment is directly related to the hydrophobicity of the compound. Thus the more hydrophobic components can be highly concentrated in sediment which can become an environmentally persistent reservoir of contaminants. The potential for accumulation in organisms is also directly related to hydrophobicity, raising concerns for the potential transfer through food chains, as well as for chronic effects such as cancer within exposed populations. In petroleum, the four- to six-ring PAHs would seem to raise the greatest concerns because of their hydrophobicity and because many of these compounds are known carcinogens and/or mutagens. Benzo(a)pyrene, benzanthracene, methylcholanthrene and benzperylene could fall into this area of concern.

One additional factor that should be considered is the possible role of components within a complex mixture that can affect the transport and bioavailability of other components of the mixture. Natural macromolecules, such as humic material, can bind contaminants, reduce binding to sediments, and reduce uptake of the bound contaminant. Components of organic-rich wastes may likewise alter environmental partitioning. In studies on the partitioning of naphthalene and methylnaphthalenes between wastewater treatment sludges and water, the oil content of the wastes was an important factor that altered expected partitioning of the PAHs to particles and water.

In summary, PAHs seem to be key components in petroleum because of their potential toxicity and relevance to human health concerns. Two- and three-ring compounds should be analyzed because of their potential for acute toxicity, and four- to six-ring compounds because of their potential for long-term bioaccumulation and chronic toxicity. The matrix of the petroleum waste may alter the expected transport and bioavailability, and may need to be considered in analyses.

## MARKERS OF PETROLEUM HYDROCARBON CONTAMINATION OF DREDGED MATERIAL \*

Crude petroleum and most refined petroleum products are extremely complex mixtures of thousands of organic compounds. Aliphatic and aromatic hydrocarbons are usually the most abundant, often representing more than 75 percent of the oil. The remainder is made up primarily of various oxygen, nitrogen, and sulfur-containing organic compounds. Any method used to monitor petroleum contamination of sediments, dredged material, or aquatic organisms must take into consideration this compositional complexity.

Most commonly used methods for estimating total petroleum hydrocarbons (e.g., infrared, gravimetric, packed column gas chromatography methods) are subject to substantial interference by non-petroleum organic materials (mostly biogenic lipids and hydrocarbons) and differentiate poorly between toxic/persistent and nontoxic/nonpersistent ingredients of oil. A method for determining petroleum hydrocarbon contamination of dredged material should focus on quantifying a subset of petroleum ingredients that possess the following characteristics:

- They are abundant in crude and refined petroleum products and rare or absent in other potential sources of environmental hydrocarbons;
- They are persistent in sediments and dredged material;
- They are highly toxic, carcinogenic, and/or bioavailable to benthic organisms;
- There are analytical methods available by which the indicator compounds can be analyzed in dredge material cheaply and unambiguously.

Two classes of petroleum components that seem to meet these criteria are phenanthrene and dibenzothiophene and their alkyl homologues. Both types of compounds are abundant in most crude petroleum and refined petroleum products, with the exception of highly refined products such as gasoline, kerosene, and jet fuel. Phenanthrenes and dibenzothiophenes are among the most acutely toxic to aquatic organisms of the major organic

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components of oil. They are not abundant in most nonpetrogenic sources of hydrocarbons. Alkyl phenanthrenes occur naturally in retene, an ingredient of pine tar. Dibenzothiophenes apparently are not biogenic and are not readily derived from biogenic precursors by short-term natural diagenic or pyrogenic processes. Both classes of compounds are among the most persistent components of petroleum in sediments. Lower molecular weight hydrocarbons are lost from sediments rapidly through solubilization and biodegradation. Higher molecular weight aromatic hydrocarbons are more persistent, but they are not well represented in crude petroleum and most refined products, with the exception of residual oil and asphalt. In addition, they are abundant in pyrogenic hydrocarbon assemblages and therefore are not good markers of petroleum pollution. Finally, both phenanthrenes and dibenzothiophenes can be analyzed routinely by gas chromatographic techniques that are not excessively difficult or costly. In the case of dibenzothiophenes, use of a sulfur-specific detector facilitates differentiation of dibenzothiophenes from naphthalenes.



REGULATORY EVALUATIONS OF PETROLEUM HYDROCARBONS  
IN DREDGED MATERIAL\*

- I. Which key petroleum hydrocarbons will be of most use in evaluating petroleum in dredged materials:

As a matter of semantics, I suggest that we not constrain ourselves by describing the compounds of interest as "petroleum hydrocarbons." Once outside the alkane groups we shall be dealing with numerous aromatic compounds which may be found as parent compounds in petroleum or petroleum products, but also may derive from pyrolysis and pyrogenesis. Indeed, we may well find ourselves devoting much of our time to aromatic hydrocarbons with sources in the ambient air as combustion products of fossil fuels, and with various aromatics arising from the discharges of industrial and solvent wastes.

- II. Are high-resolution, specific analyses to identify individual hydrocarbon components desirable in any case:

In most cases such analyses are probably unnecessary. There are lots of instances in the literature that show that the accumulation of normal alkanes and many cycloalkane compounds is relatively unimportant in terms of overall toxicity to the resident biota or to humans consuming fisheries products containing such compounds. Tainting of fish flesh is a different story, and is widespread; however, I don't think enough is known about the compounds responsible for such tainting to include them in our discussions at any length.

Most attention should be given the aromatic and polyaromatic compounds known to accumulate in sedimentary material in the vicinity of urban-industrial regions. This approach, however, does not result in enough reduction of complexity. From the data

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presented by MacLeod et al. (1981) for the New York Harbor and Bight region, one might expect in excess of 100 hydrocarbon compounds to show up in broad-scan analyses. Bieri et al. (1982) identified 300 to 400 aromatic compounds in the sediments from the Elizabeth and Patuxent Rivers and estuaries in the Chesapeake system. Jim Lake and colleagues have had similar results in their analyses of sediments from Black Rock Harbor. If one were to assume (conservatively) that sediments from an urban estuary may contain about 200 aromatic compounds the analytical cost is still way out of hand, and the interpretation of such data remains nearly impossible.

Precisely which aromatic hydrocarbons should be considered as "important" is a difficult question to answer. One would like to suggest those compounds with the potential to cause acute lethal effects or chronic toxic responses (carcinogenicity, mutagenicity) in aquatic organisms, laboratory animals or in humans. This would narrow the list considerably, and this is my personal recommendation. However, discovering which compounds have the aforementioned actions may be a very large task. It might be suggested, therefore, that we proceed with the use of the compounds known to accumulate or to have the potential for unacceptable acute and chronic effects; viz.: BAA, DMBA, PHE, BaP, the dibenzpyrenes, benzophenanthrenes, ANT, and a few others. Refinements of this approach will come with time and understanding.

Two approaches present themselves at this point. First, one might analyze sediments for a restricted number of aromatic hydrocarbons using routine procedures of extraction and analysis by GC and GC-MS. Second, one might perform a simplified separation into hydrocarbon classes using a two-step procedure of a) extraction, and b) thin-layer separation of compound classes within the original extract. The second approach may be the more economical and the more satisfying scientifically because you would end up with a screen of sediments for a number of classes, as well as the separation of the PAH class.

Once compound classes have been separated using the second method, TLC plates may be scraped and analyzed for identification of key hydrocarbon components on HPLC or HPLC-MS. On a system in use in our lab, for example, TLC runs of cyclohexane-extracted sediment accomplish the separation of multi-aromatic hydrocarbons from nitro-aromatics and other compound classes. Subsequent HPLC analysis is simplified by the prior removal of compounds which normally "mess up" a GC run. Identification of compounds on HPLC is relatively easy using known standards and verification on MS. HPLC-MS is not required; fractions can be collected easily from the HPLC and run on GC-MS. Fraction collection from a GC is difficult.

### III. What do you do with the identification-concentration data collected through analysis:

Some protocol must be established in order to evaluate the bioaccumulation or the toxicity/potential toxicity of the compounds identified from analysis of a sediment. Many have been suggested; these include 1) direct bioassay, 2) calculation of the disposition of compounds among environmental media (Mackay and Paterson, 1982); 3) condemnation of sediment based upon the presence of carcinogenic or mutagenic compounds therein, and 4) estimation of the bioconcentration factor for compounds of interest based upon physical parameters such as solubility, log P, parachor, molecular connectivity and other parameters of QSAR (Koch, 1984).

Direct bioassay methods are most advisable, but probably impractical. Certainly there is evidence that the PAHs are accumulated by organisms in contact with PAH-contaminated sediments. However, studies done by almost everybody in the workshop group have shown that many of the polyaromatic compounds are metabolized so rapidly that one has little hope of finding the parent compound in an organism from an environmental sample (Lee et al. (1972) for naphthalene; Varanasi and Gmur (1981) for BaP and naphthalene; Moese and O'Connor (1985) for phenanthrene; general effects

found in Whittle et al. (1977) and Brown and Weiss (1978). To a large extent this leaves routine bioassay out as a means for evaluating the sediment; however, routine bioassay could be done as long as you look for the metabolites and not the parent compound. Whether this is practical is a matter for lengthy discussion.

The rest are all indirect methods. They suffer from a general lack of realism; for realism see Califano's paper (Califano et al., 1982) on suspended solids reducing bioaccumulation of PCBs, and McCarthy's paper (1983) on particulate material decreasing accumulation of PAH in Daphnia.

The proposed BCF approaches include the caveat that estimation of BCF from "stock formulae" is made less reliable for compounds subject to metabolism (Mackay, 1982). I should suggest that Mackay and his colleagues, in their various publications on the Fugacity Model and the prediction of bioaccumulation from physical parameters, may be underestimating the value of some of the equations derived for BCF calculations (Mackay, 1982; Mackay and Hughes, 1984). In particular, when you compare the sorts of manipulations performed in the Mackay and Hughes (1984) paper, and relate them to QSAR or QSPR approaches (QSPR = quantitative structure-pharmacokinetic relationships) (Mackay and Shiu, 1984; Mayer and van der Waterbeemd, 1985) you find lots of potential to account for metabolism within the BCF concept.

Once we have arrived at reasonable conclusions regarding which compounds should be given the most attention, we should proceed to develop an understanding of their distribution in the environment through approaches like the Fugacity Model, and we should develop an understanding of their potential for accumulation and metabolism in organisms through QSAR and QSPR. The Fugacity Model is developing rapidly due to the attention given by Mackay and his co-workers. QSAR and QSPR need a great deal more attention from toxicologists and environmental chemists; a means for supporting development in this area should be found.

#### IV. Summary

- A. It is my feeling that we should be concentrating on the aromatic hydrocarbons, particularly those that are known to have acute and chronic effects in aquatic biota, on laboratory animals and on mammals. Specifically, the PAHs. Aromatic hydrocarbons of concern should also include those that have been shown to cause a positive response (+S9) in the Ames mutagenicity assay.
- B. In-depth analysis of dredged material for aromatic hydrocarbons is ill-advised due to its expense and the uninterpretable amount of data which are produced. I would suggest as an alternative a screening approach in which chemical compound classes are separated prior to analysis, and that analysis be restricted to a limited number of compounds. Fractions from HPLC analysis may be collected for future reference if such seems advised.
- C. If screening and identification analyses show the presence of candidate hazardous compounds, then bioassay should be conducted. Bioassays must be performed with the understanding that parent compounds are unlikely to be found; analyses will have to be for metabolic products. Is this useful?
- D. Evaluation of the data obtained through limited analysis for PAH compounds and bioassay may be accomplished using a variety of mathematical models predicting:
  1. Distribution within environmental compartments. Compounds with a high probability of accumulating in biota should be flagged.
  2. Bioconcentration by fishes and the potential for transport to the human population (QSAR; QSPR).
  3. The extent to which PAH may be metabolized in fishes, and the likelihood of the formation of potentially harmful metabolic products (QSPR).

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## Petroleum Residues In Sediment\*

The question of defining the possible impacts of petroleum-derived residues in dredge materials is extremely complex. It involves not only the analytical determination of these residues but must also address the bioavailability and toxicological consequences of disturbing the sediments containing these residues. For obvious reasons, simply performing an oil/grease analysis is insufficient to define the environmental impact of dredging operations.

Concerning the determination of petroleum-derived residues, one possible set of marker compounds is the priority pollutant hydrocarbons: acenaphthene, acenaphthylene, anthracene, benzo(a)anthracene, benzo(b)fluoranthene, benzo(g,h,i)perylene, benzo(k)fluoranthene, benzo(a)pyrene, chrysene, dibenzo(a,h)anthracene, fluoranthene, fluorene, indeno(1,2,3-C,d)pyrene, naphthalene, phenanthrene, pyrene. These sixteen PNAs are of interest for a variety of reasons, but most importantly a broad data base exists on effects and analytical procedures for detection of these compounds. As a starting point, these compounds offer many advantages. They may well be, however, insufficient to define the potential environmental impact of dredging operations.

The alkylated analogs of these contaminants as well as heterocyclic PNAs are known to be derived from petroleum. Considering the carcinogenic potential of these alkylated analogs and the apparent widespread occurrence of tumors in fish populations, the priority pollutant list should be expanded to include representatives of the

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alkylated and heterocyclic PNAs.

The question of bioavailability and toxicological consequences of dredging sediments may well require long-term toxicity studies, particularly if the genotoxic effect of contaminated sediments is addressed. One approach, of significantly shorter duration than the classic chronic toxicity test, is to use on-site toxicity testing. This could be modeled after the "mini-chronicity" system developed by EPA. Additionally, detection of PNA-DNA adducts in aquatic organisms is potentially possible, resulting in unequivocal evidence of genotoxic effects.

In summary, the question of defining the potential for adverse effects of petroleum-derived contaminants in sediments is an extremely complex matter. Both a validated analytical approach and concomitant toxicological assessment would be desirable.



# Suggestions for WES Workshop\*

In response to your request, I would like to offer suggestions for discussion at the workshop. The problem of adequate analysis of dredge spoils for hydrocarbons that are of environmental concern is not a simple matter. There are, however, some considerations that could help guide the discussion of which specific compounds will be of most use in evaluating the potential hazard associated with dredge spoils.

- 1) The question of which compounds are most likely to be good "indicators" will be confounded to some degree by the variation in sediment type and organic content, which could dictate bioavailability of a given compound. Thus, the availability of compounds identified in the workshop should be considered in light of the sediment type, and a recommendation might be that the content of hydrocarbons in pore water be analyzed as an indication of the availability of those compounds. The compounds then to be considered should be selected on the basis of relevance to indicate petroleum, persistence and bioaccumulation potential.
- 2) Relevance to Petroleum: If the goal is to consider petroleum only, then compounds to be examined must be clearly of petrogenic and not of biogenic or pyrogenic origin. Thus, the origin of candidate compounds must be considered. Some sulfur-compounds are known to be prominent in petroleum (e.g. thiophenes), but studies on their metabolism and persistence are few. Indicator compounds might include aromatic hydrocarbons that are known to be more associated with petroleum than pyrogenesis, at extremes of  $P_{ow}$  and rates of metabolism, and some clearly petrogenic heterocycles.
- 3) The bioaccumulation potential is in part determined by hydrophobicity, reflected in octanol-water partition coefficient, and in part by the persistence in tissues and the rate of metabolism. Accordingly, it might be suitable to analyze the tissues of test organisms held in pore water or above a sediment water interface for the presence of available indicator compounds. Alternatively, the compounds or their metabolites could be examined in the bile of selected fish species. Detailed studies on biotransformation of selected compounds would be recommended, where such data do not exist.
- 4) In considering the approach to monitoring, it would be appropriate to examine the tissue, and/or bile, both for petroleum indicator compounds, and for other compounds known to be biologically important, including aromatic hydrocarbon carcinogens. In addition, it would be helpful to evaluate some biological effect associated with these compounds, by examining, for example, the levels of cytochrome P-450 induction in appropriate test organisms exposed to the dredge spoils.

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- 5) In order to properly evaluate the significance of petroleum compounds, it would be necessary to consider the content of other hydrocarbon compounds and particularly chlorinated organics in the same sediments. If the concern is for environmental effects of the dredge spoils then consideration of other agents which might adversely impact animals in the vicinity of such sites would be necessary.

## Regulatory Identification of Petroleum Hydrocarbons in Dredged Material\*

The emphasis of the workshop should be on the polycyclic aromatic hydrocarbons for the following reasons: (1) the mono- and diaromatic hydrocarbons, which appear to be the most acutely toxic from petroleum, are generally not found in significant concentrations in sediment, (2) because of the hydrophobicity of the high molecular weight PAH they avidly bind to particulate matter, making sediments a major reservoir for these hydrocarbons, (3) many of these PAH are known or suspected mutagens and carcinogens, (4) they have the potential to accumulate in certain aquatic species and (5) there has been extensive work on the analysis for these hydrocarbons in sediment, as well as studies on their bioavailability to and metabolism by several aquatic phyla. Therefore, the following compounds may be suggested as key PAH for evaluation of dredged material: phenanthrenes [ratio of alkylated derivatives to parent hydrocarbon would give useful information as to source (i.e., petrogenic vs pyrogenic) of contamination], benz(a)anthracene (moderate carcinogen), chrysenes (certain methylated derivatives are carcinogens), benzo(a)pyrene (potent carcinogen--extensively used as a model PAH in bioavailability and metabolism studies), benzo(e)pyrene (a cocarcinogen), benzo(a)fluoranthene (certain isomers are carcinogens) and dibenz(a,h)anthracene (strong carcinogen). Additionally, heteroatom polycyclic aromatic compounds may be considered, such as azaarenes and nitroaromatics. These compounds are generally minor components of petroleum, but are formed during pyrolysis and constitute an important class of known or suspected mutagens and carcinogens.

However, the evaluation of dredge material is a complex issue and analyses of only a few samples for specific PAH may not give adequate information to make a regulatory decision. The following additional factors need to be

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considered: (1) the heterogeneity of the level of contamination of dredged material, (2) the influence of sediment composition (e.g., organic carbon content) and (3) the source of the contamination on the bioavailability of the contaminants. It may be useful to consider the use of a quick general method to estimate the level of PAH present, in order to assess the overall contamination, then use more sensitive techniques, such as GC and GC/MS, to determine the concentration of the indicator PAH in selected samples. Further, the identification and quantification of indicator PAHs in dredged material without an assessment of bioavailability and toxicity, acute and chronic, is of limited usefulness. Though much work is being done to develop structure-activity relationships (SARs) to predict toxicity and accumulation potential, the complex and variable nature of dredged material is such that biological tests are still necessary to complement the SAR predictions. The workshop should discuss which tests give the most information on the bioavailability and toxicity of PAH associated with dredged material.

## REGULATORY IDENTIFICATION OF PETROLEUM HYDROCARBONS IN DREDGED MATERIALS

The fate and transport of petroleum hydrocarbons in sediments are controlled by the physical and chemical properties of the sediment environment and the intrinsic properties of the compounds themselves. The fate processes that are generally incorporated into exposure analysis modeling are thermal reactions including hydrolysis and redox reactions, photolysis including direct and indirect processes, sorption, volatilization and biodegradation. The selection of compounds or classes of compounds for estimating the environmental impact of petroleum hydrocarbons should take into consideration these fate and transport processes.

The feasibility and expediency of both qualitative and quantitative analysis should also play an important part in selecting specific compounds. This includes procedures for sampling of sediments, analysis of the aqueous phase as well as development of extraction procedures for the solid phase and subsequent analysis. Possible considerations in analysis include separation of the saturated hydrocarbons from the aromatics by column chromatography followed by analysis of the non-polar compounds by capillary gas chromatography, and analysis of the polar compounds by high pressure liquid chromatography. This should provide straightforward and relatively inexpensive sample workup and analysis.

Compounds to be monitored should include a large cross section of physical and chemical properties. These should include four or five homologous normal or branched alkanes spanning a large range of chain length, and thus sorption and biodegradation properties. These should also include four or five homologous polynuclear aromatics with increasing numbers of fused ring aromatic moieties to cover a wide range of molecular weight and thus physical properties. Three or four polar heterocyclic compounds should also be monitored. The compounds from these groups should be selected based on bioavailability, toxicity and frequency of occurrence. In addition, monitoring the ratios of the compounds in a homologous series will provide insight as to the physical and chemical properties that are responsible for the fate of the petroleum hydrocarbons. This will provide some basis for extrapolating exposure concentrations for other compounds.

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## APPENDIX C: WORKSHOP EVALUATION

1. At the close of the technical discussions, the workshop participants were asked to rate the success of the workshop on seven evaluation factors using a ranking of 1 (low) to 5 (high). These factors and their summary statistics are presented in Table C1.

2. Reactions were generally favorable, and overall the workshop was deemed a success.

Table C1  
Summary of Workshop Evaluations

Evaluative Factor	No. of Responses		Mean	Range	Comments from Participants
1. The purpose and objectives of the workshop were clearly stated.	15	4.3	3-5		
2. The preworkshop inputs were useful and worthwhile.	15	3.9	3-5		
3. The structure of the workshop (i.e., short topic introductions followed by roundtable discussion) was the best format to achieve the objectives.	15	4.1	2-5		<p>"An acceptable format for sure, but I can't say the BEST."</p> <p>"It did help stimulate discussion."</p> <p>"The second day format was more useful."</p> <p>"Data presented in overviews was commonly already known by participants."</p>
4. The objectives of the workshop were met.	15	4.2	2-5		<p>"While a list was prepared, I wonder if a tiered protocol was agreed on? I believe sediment analysis must be included and reproductive and carcinogenicity/mutagenicity testing must be included."</p>
5. The Monday evening plenary session was worthwhile.	14	3.5	1-5		<p>"The arrangement of the tables really limited the opportunity for people to get to know each other. If the table arrangement had been</p>

(Continued)

Note: Factors were ranked on a scale of 1 to 5, where 5 equals "Strongly Agree" and 1 equals "Strongly Disagree."

Table C1 (Concluded)

Evaluative Factor	No. of Responses	Mean	Range	Comments from Participants different, the rating would have been higher."
5. The Monday evening plenary session was worthwhile. (Continued).				"Poor table arrangements--limited opportunity for interaction."
6. The length of the workshop was appropriate.	15	4.2	2-5	"2 days would have been enough."
7. The workshop was worth the trip to Vicksburg.	14	4.3	3-5	"Add 1 day."



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